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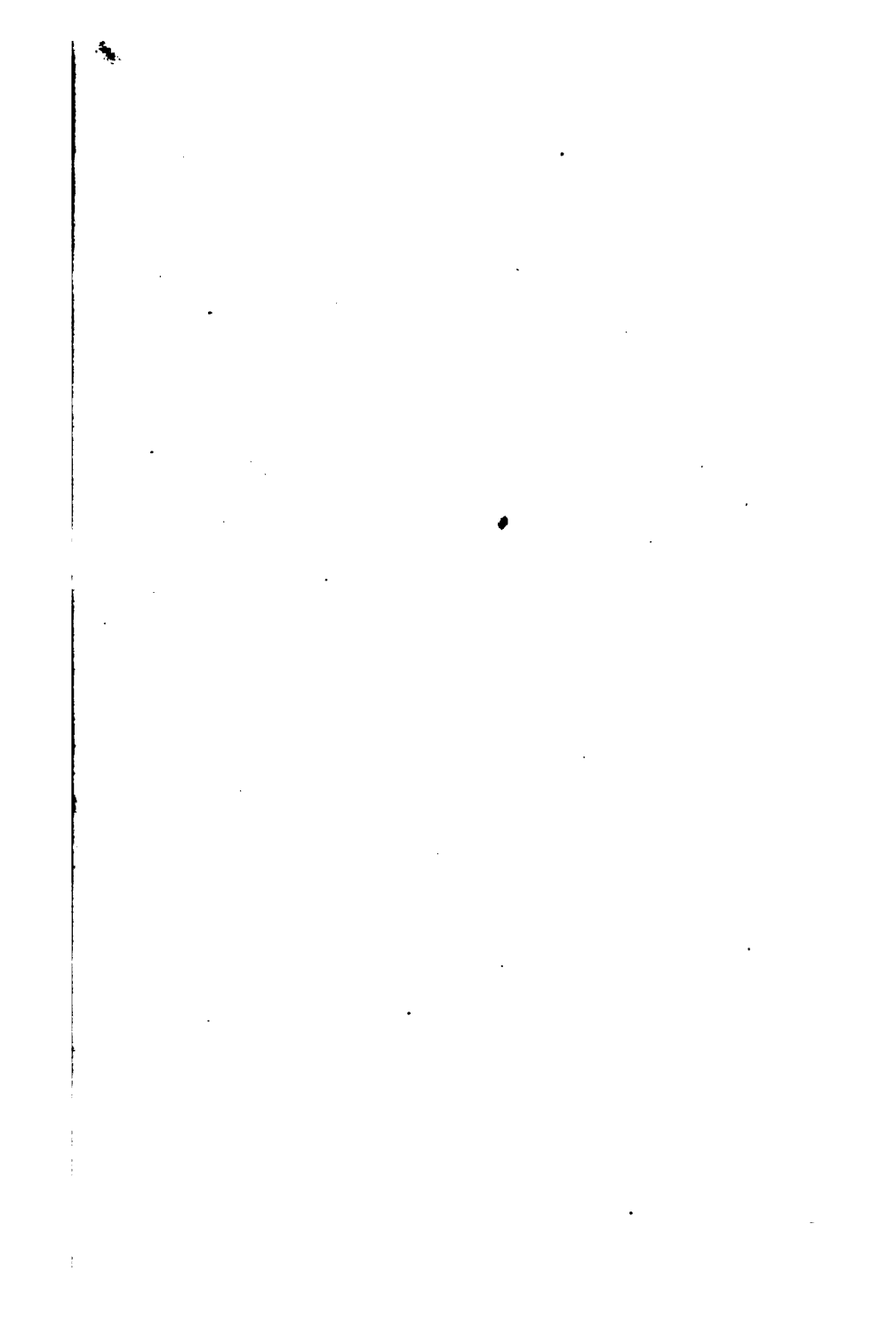
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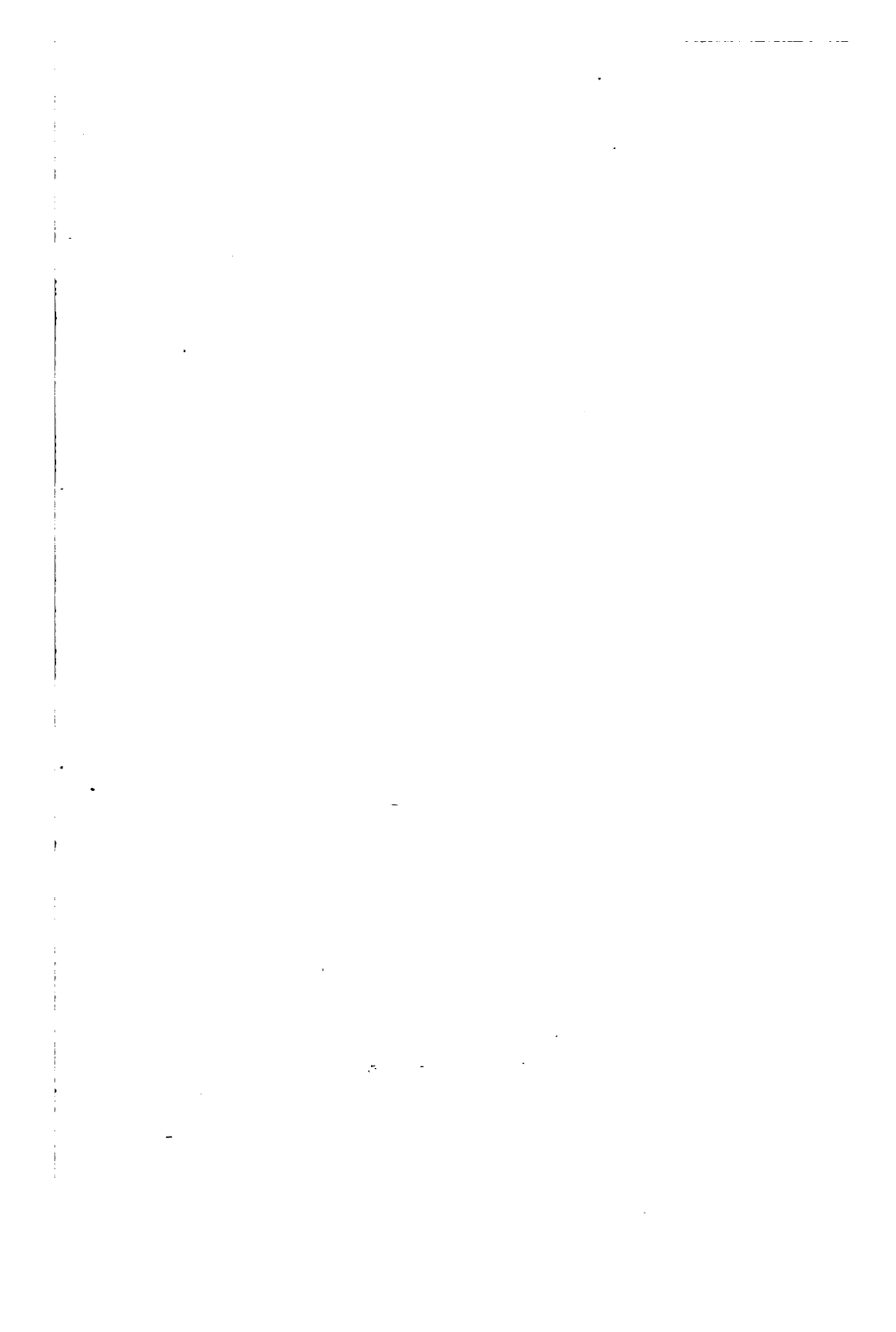
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# INTRODUCTION

TO THE STUDY OF

# CHEMICAL REACTIONS.

BY

DR. PHIL. EDMUND DRECHSEL,

PROFESSOR OF PHYSIOLOGICAL CHEMISTRY AT LEIPZIG UNIVERSITY.

TRANSLATED, WITH PERMISSION OF THE AUTHOR AND OF THE  
PUBLISHER, AND SPECIALLY ADAPTED TO THE USE OF  
AMERICAN STUDENTS, BY NOTES, ETC.

BY

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## AUTHOR'S PREFACE.

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IN this *introduction* I have endeavored to supply the student with whatever may be of service in assisting him to a clear comprehension of chemical processes. I have not restricted myself, therefore, to a mere expression of the reactions by equations, but have preceded these with the shortest possible presentation of the most important considerations which form the foundation of our present theoretical views.

I have chosen the rational formulas for the equations in order to give to the student a definite nucleus around which to cluster his ideas of the recondite changes which occur in chemical reactions.

DR. E. DRECHSEL.

## TRANSLATOR'S PREFACE.

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I WAS led to translate this elementary treatise upon chemical reactions by the belief that it would be a convenient auxiliary to studies within the limits of elementary general chemistry and elementary qualitative analysis. This opinion was founded upon my own use of the book and upon that of fellow-students.

In translating I have endeavored to represent the original text of the author truthfully, but upon this subject I would call attention to the following points :

1) Everything pertaining to chemical terminology, in its widest sense, I have regarded as matter not for strict translation, but which should be rendered in the most advanced scientific terminology adopted in our own country at the present time ; so that I have taken the greatest liberties in this respect.

2) All insertions in the text which are inclosed in brackets, [    ], are interpolations made by the translator.

3) The translator alone is responsible for all of the foot-notes, the prefatory note of explanation and for the table of contents.

The book was originally published by the firm of Johann Ambrosius Barth, at Leipsic, bearing the title: "Leitfaden in das Studium der chemischen Reactionen."

N. F. M.

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## EXPLANATORY NOTES.

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SINCE this book may fall into the hands of some who are not familiar with its system of formulas, these few explanations are made in order that no doubt may occur to such concerning the indicated structure of the compounds considered. These explanatory remarks should be read in connection with pages 8-15 of the text.

Roman numerals at the right of a letter, or group of letters (in these remarks the words *letter* and *letter-group* are used for the represented *atom* and *atom-group*) indicate the *valence* of the atom, or atom-group thus represented; in this work, univalence and bivalence are indicated by marks like minute and second marks, respectively. If such valence marks apply to an atom-group, the atom-group is placed in a parenthesis: C<sup>iv</sup> indicates one

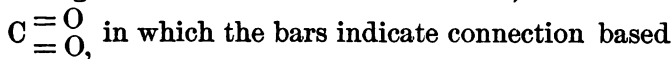
atom of quadrivalent carbon; but  $\left( \begin{array}{c} \text{Fe}^{\text{iv}} \\ || \\ \text{Fe}^{\text{iv}} \end{array} \right)$  indicates

a quadrivalent atom-group made up of two atoms of quadrivalent iron connected together by two valence

units of each atom ; therefore, four valences remain for the atom-group as a whole.

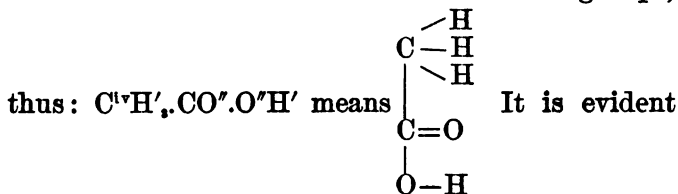
A large Arabic numeral at the left of a formula affects the whole of such formula without regard to the points occurring between certain letters and letter-groups, excepting in the few cases of some *double salts* and other *molecular additions* (see p. 66); in these exceptional cases, such a numeral affects the formula, commencing with the letter following the numeral, only as far as to the next point :  $8 \text{ NO}_2.\text{O.H}$  means  $8 (\text{NO}_2.\text{O.H})$  ; but  $4 \text{ Fe Cy}_2. 3 \text{ Fe Cy}_2$  (p. 137) means four times the group  $\text{Fe Cy}_2$ , combined with three times the group  $\text{Fe Cy}_2$ .

The points occurring serve to indicate the supposed grouping of the atoms in the given molecule, and in all cases, excepting the few cases of "molecular addition" (p. 66), they also indicate, taken in connection with the valence marks, the arrangement of the atoms and atom-groups. Let us consider this more closely : a point occurring between two single letters indicates that two such letters are joined together, thus :  $\text{H.O.H}$  means H to O and O to next H ; but a point occurring between a single letter and a group of letters means that the single letter is connected to the *group* ; to which particular letter of that group is rendered evident by the valence of the atoms, thus :  $\text{C}^{\text{I}}\text{O}^{\text{I}}.\text{O}^{\text{I}}$  does not mean that the two O's are directly joined together, but indirectly through the mediation of the atom of C, as follows :



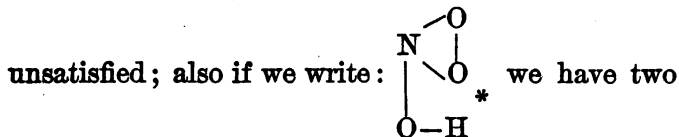
upon valence units, we might say : *valence connections*. The same regard to the valence of the atoms

will render plain the indicated connections when a point occurs between two polyatomic groups, or when a formula is divided into several such groups,



that such formulas may become inconvenient in a book specially intended to be comprised within as narrow confines as possible, and that they may be rendered wholly unnecessary by such simple devices as those adopted in this book and so often elsewhere.

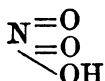
But the student may find still other instances wherein there seems to lurk some ambiguity. For instance, in a formula like the following:  $\text{N}^{\text{O}}\text{O}'', \text{O}''.\text{H}'$ , evidently H is connected to O and this O to the group  $\text{NO}_2$ , either to one of the O's of the  $\text{O}_2$  or else to the N; but further, how are the O atoms of the group  $\text{NO}_2$  arranged? Are they connected directly with each other or only indirectly through the mediation of the N? Here again the valences settle the question. It is seen that N has five valence units to be satisfied; if we were to write:  $\text{N}-\text{O}-\text{O}-\text{O}-\text{H}$ , four valences of N would be left




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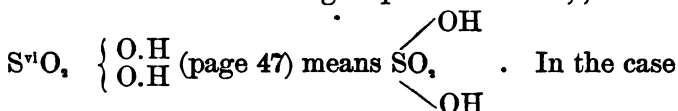
\* This structure formula for nitric acid is advocated by some writers. Its adoption involves the trivalence of the nitrogen atom.

valences of N unsatisfied; the same is true if we write:  $\text{N} \begin{smallmatrix} =\text{O} \\ -\text{O}-\text{OH} \end{smallmatrix}$ . Finally it is plain that the only structure which satisfies the conditions is:



It should be remembered by the beginner that in every such case of connection between two atoms as the following:  $\text{H}-\text{H}$ , the bar represents one satisfied valence unit for *each* atom.

One more device remains to be noticed,—the brace  $\{$ . The single brace does not indicate that the atoms or atom-groups which it ties are directly connected with each other, but indirectly through direct connection with the atom or atom-group outside of it (this when no point intervenes between brace and atom or atom-group outside of it); thus:



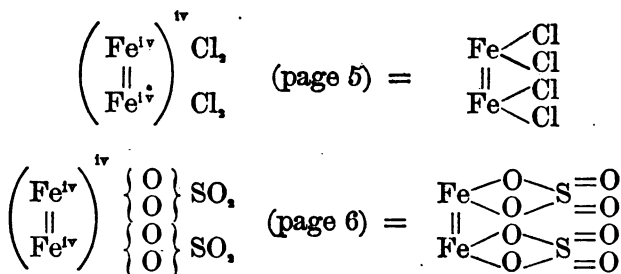
of a double brace, each part of it is to be similarly interpreted:  $\text{Ca}'' \left\{ \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right\} \text{SO}_2$  (page 109) means

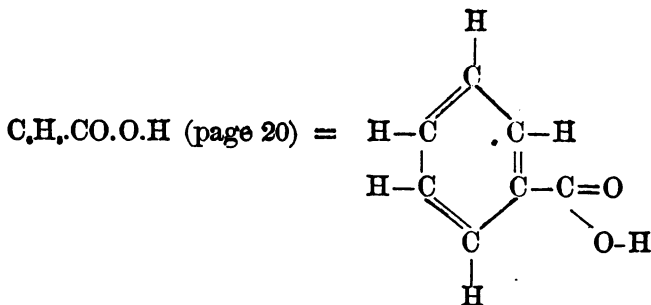
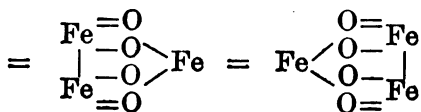
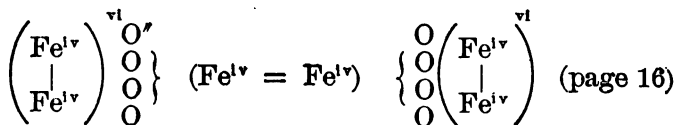
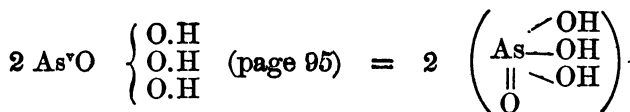
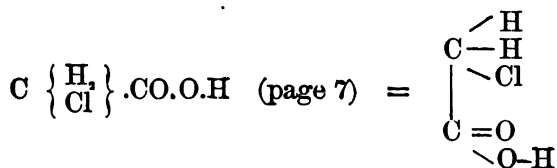
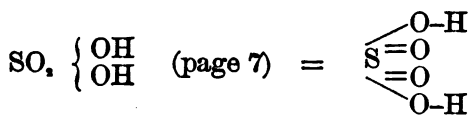
$\text{Ca} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{SO}_2$ . The double brace is sometimes employed as common parenthesis or bracket (p. 102), where its sense is evident.

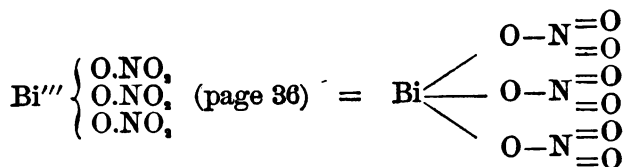
Whenever connecting bars are employed, they not only represent connections depending upon valence,



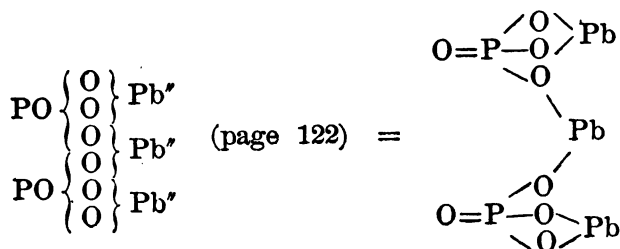
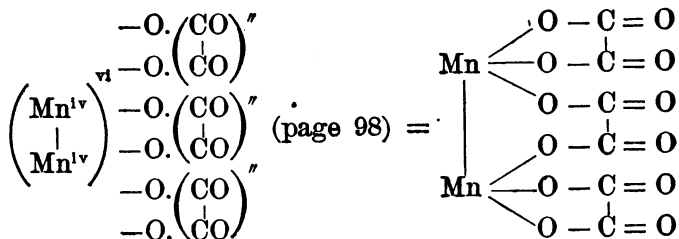
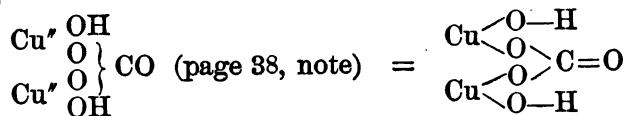
as do all of the devices above considered, but they indicate by their number the number of valence units so satisfied; in this respect they perform more than the points, unless, as is frequently done, points be used exactly as bars are used, in which case they also indicate by their number, directly, the number of valence units which they represent (see note, p. 99). Thus, in  $\text{Ca}^{\cdot}\text{O}$  and  $\text{Ca}=\text{O}$ , both the point in the one, and the two bars in the other, formula indicate a connection based upon valence, but the point expresses the matter less completely than the two bars, since the latter show *how many* valences (two of each atom) are satisfied; in the form  $\text{Ca}^{\cdot}\text{O}$  it really requires the point and the valence marks to do as much. Valence numerals are customarily omitted, in this book in many cases, where familiarity renders their insertion superfluous. Likewise the point is often omitted in familiar connections within familiar groups, as in  $\text{OH}$  for  $\text{O.H}$ ; so in  $\text{NO}_2.\text{OH}$  for  $\text{NO}_2.\text{O.H}$ , etc. It is believed that the foregoing remarks, together with the following examples taken from the text, will make the system adopted in the book perfectly intelligible to the beginner, even for cases which it did not seem necessary to notice specially:







(See note, page xvii of these notes.)





# DRECHSEL'S INTRODUCTION.

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## MOLECULE; ATOM.—REACTIONS.

WHEN we divide a compound substance mechanically we always obtain only smaller parts of the same substance, possessing the same composition and all of the same properties which characterized the original compound. We can conceive of continuing this process of division until a limit is reached, beyond which, were further division to be made, we should not obtain parts of the same kind. This division, however, cannot be accomplished by mechanical means, but only by chemical agency. For example, if we pulverize mercuric oxide as finely as it is possible for us to do, we shall still see under the microscope only distinct grains, all of a kind. If, on the contrary, we heat the same substance sufficiently, we observe that the mercuric oxide suddenly vanishes, and that in its place two substances appear—mercury and oxygen. Consequently the mercuric oxide, each smallest part of it, must have resolved itself into these two substances, which, therefore, must have been contained in each of those smallest parts of the substance designated mercuric oxide. These smallest mass-parts which cannot be further mechanically divided but

only chemically, and which then separate into unlike parts, are named molecules (or physical atoms), while their component parts are called atoms (chemical) when these are single, and atom-groups or radicals (compound) when they are again compounded. The simple atoms are not further divisible either by chemical or mechanical means. Certain facts compel us to assume that the smallest mass-parts, or molecules, also of simple bodies, *i.e.*, of such bodies as cannot by any means be separated into unlike components, consist in most cases of at least two atoms which are alike *inter se*.\*

It is clear that the customary definition of molecule as the smallest quantity of a substance which is capable of existence in the free state accords fully with that given above, the mode of its deduction simply being somewhat different.

It is these molecules among which, and through the reciprocal workings of which, the phenomena are produced which we call chemical processes, or in general, reactions. If we investigate the composi-

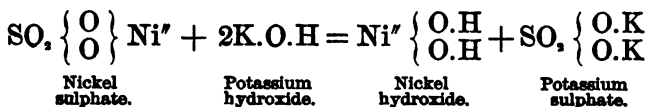
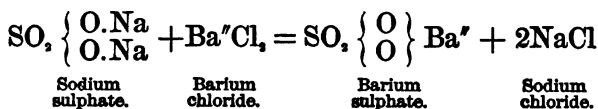
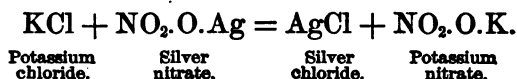
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\* The molecules of cadmium and mercury in the state of vapor are regarded as consisting of only one atom. In the case of mercury, special evidence in support of this view has been adduced from the determination of the velocity of sound in mercury vapor, indicating that there is no intra-molecular motion, and hence the molecules do not consist of several smaller parts (atoms) free to move about each other. (Pogg. Ann., 1876, Bd. 157, S. 353.)

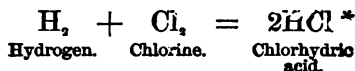
The vapor densities of arsenic and phosphorus indicate four atoms to the molecule, while sulphur at a temperature above 800° C. appears to possess two, and at about 500° C. six, atoms to the molecule.

tion of those molecules which were present before the advent of a chemical reaction, as well as of those newly formed molecules found to be present after its completion; and if we compare, further, the results thus obtained, we shall find that the chemical process, the reaction, between the unlike molecules consists simply herein: that the atoms, atom-groups or radicals which constitute the molecules separate from each other and then reunite, forming new, differently constituted molecules; and further, that the sum of all of the atoms which take part in the reaction is unchanged hereby, while the sum of the molecules before the reaction may be different from that after. According to the changes in the composition of the molecules present brought about by the reaction, the following distinctions among chemical processes may be made:

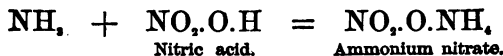
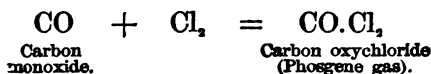
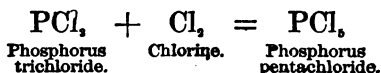
1) *Double or reciprocal decomposition*, mutual exchange of two atoms or atom-groups; under this head belong such reactions as the following:



Here should be classed also direct combinations of two elements, processes which may be represented as simple additions and which were formerly regarded as such :



2) *Simple addition*, direct union of two or more molecules forming a single one :



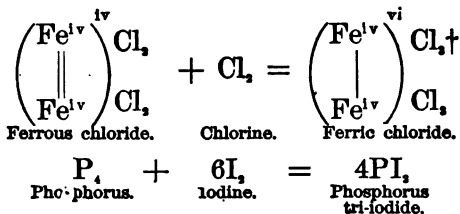
3) *Addition accompanied by the breaking up of one or more molecules* ; here belong some oxidation processes and direct unions ; the number of mole-

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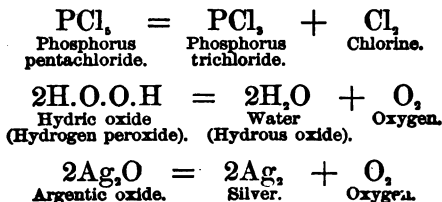
\* Thus :  $\text{H.H} + \text{Cl.Cl} = \text{H.Cl} + \text{H.Cl}$



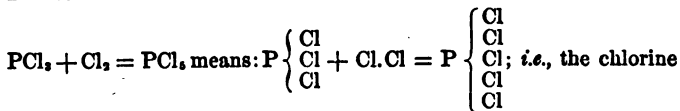
cules present after the reaction is smaller than before it.\*



4) *Simple resolution of one or more molecules into two or several molecules :*

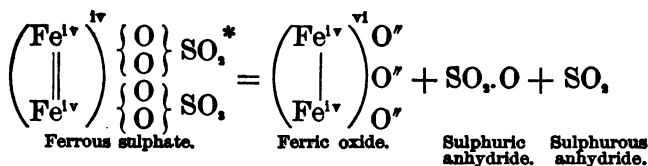
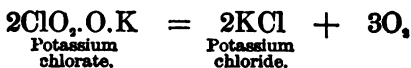


\* This really includes the preceding case 2), since in the examples falling under it one of the combining molecules is broken up, and the number of molecules after the reaction is less than before it:

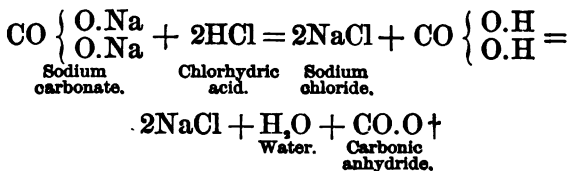


molecule is sundered, etc.

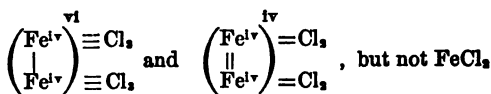
† Such reactions as this one are often, and not improperly, written in the simplest stoichiometric proportions, thus :  $\text{FeCl}_3 + \text{Cl} = \text{FeCl}_4$ ; only we should remember that this latter form does not express molecular weights. But when for the ferric chloride the molecular weight of the vapor,  $\text{Fe}_2\text{Cl}_6$ , is written,  $\text{Fe}_2\text{Cl}_6$  should be written for the ferrous chloride. Strangely enough this point is not always observed and the consequence is a vicious one, since the simultaneous employment of the formulas  $\text{Fe}_2\text{Cl}_6$  and  $\text{FeCl}_3$  would indicate that, by the conversion of the ferric into the ferrous chloride, a fundamental breaking up of the molecule occurs, while in reality, at the most, the reverse is true. (See Lothar Meyer, "Die Modernen Theorien der Chemie," 8te Aufl. S. 231.)



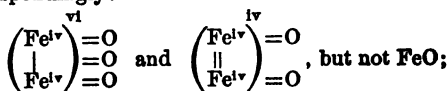
Here belongs also the case of the immediate decomposition of a molecule issuing from a reaction by double decomposition :



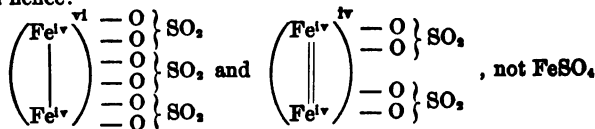
\* It may be noticed that this is not the formula usually written for ferrous sulphate,  $\text{FeSO}_4$ , but its double. If, however, molecular weights are to be represented, and if, for iron compounds, we wish to write formulas which shall not be inconsequential (see note on page 5), we should assume for ferrous sulphate a mol. wt. at least as large as  $\text{Fe}_2\text{S}_2\text{O}_8$ , if we write  $\text{Fe}_2\text{Cl}_4$ ,  $\text{Fe}_2\text{Cl}_6$ , etc. Thus :



and, correspondingly:

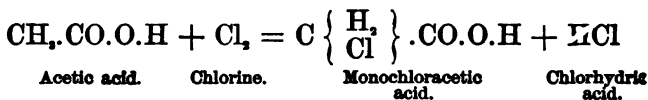
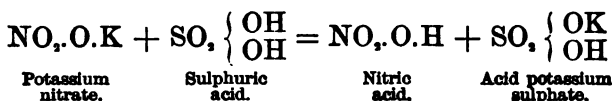


and hence:

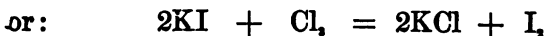
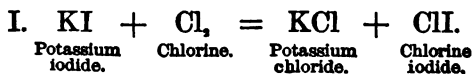


† In general, the combination of two groups of OH (hydroxyl) to one and the same carbon atom is maintained with difficulty.

There are still other reactions which appear to be somewhat peculiar, as the expulsion of one element from its position by another, or substitution ; upon closer inspection, however, it is found either that such reactions are simply cases of mutual exchange :



or, as it is customarily expressed, that they take place in two stages, *i.e.*, the molecules formed by the first reaction immediately enter into a new reaction, and hence not these molecules but the products of this second reaction first become perceptible to us. For instance, the expulsion of iodine by chlorine :



The instance, cited above, of the decomposition of sodium carbonate by chlorhydric acid belongs here, inasmuch as the carbonic acid [dibasic carbonic

acid], separated at first, immediately decomposed into water and carbonic anhydride.

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### VALENCE OF THE ATOMS.

THE smaller parts into which we divide the molecule by chemical agency are either simple, so-called elementary, atoms; or radicals, that is to say, groups of atoms. In the following discussion we shall first consider the former kind. Since we cannot further decompose these atoms, either by mechanical, physical or chemical means, we must assume that these atoms as such, as totalities, as integers, enter into chemical combinations and continue to exist in these. It follows from this that the weight of a molecule is equal to the sum of the weights of the atoms constituting it; and further, that these atoms combine among themselves in quantities which represent multiples, in whole numbers, of the weights of the individual atoms themselves. This is nothing else than the law of multiple proportions. If we know that a molecule M consists of  $a$  atoms of an element A, and  $b$  atoms of an element B, and if, further, the weights of each atom of A and of B referred to the same unit are related to each other as  $p:p'$ , then is the weight P of the molecule M:— $P = ap + bp'$ ; if then  $c$  atoms of the element C of an atomic weight  $p''$  enter into the combination, we have:

$$P' = ap + bp' + cp'', \text{ etc.}$$

We do not know the cause of the combination of two atoms with each other ; in order to explain the matter to ourselves plausibly we assume a peculiar power of attraction, chemical affinity, which is at work between the atoms and binds them together into molecules. The nature and working method of this force are wholly unknown to us. For our purpose it is quite sufficient to acquaint ourselves with a single property of this force which is revealed by a comparison of the composition of different molecules. We find that the atoms of two elements, for the most part, can unite with each other not only in one single proportion but in several. For example, tin and chlorine form both the compounds stannous chloride and stannic chloride by the union of

1 at. tin + 2 at. chlorine = 1 mol. stannous chloride.\*

and,

1 at. tin + 4 at. chlorine = 1 mol. stannic chloride.

A number of other elements behave similarly ; for instance, iron, copper, platinum, etc. ; one atom of each of these substances can unite with chlorine in more than one proportion, an assumption the correctness of which is proved by the existence of two or more compounds of the same metal with chlorine. There are substances, however, whose atoms can combine in only one proportion with each other. If

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\* See note, page 12.

we choose as unity the chemical atom-fixing power of an atom which is not in condition to bind more than one atom of any other element, and refer to this standard the amount of chemical atom-fixing power of any other atom, we obtain its atom-fixing power or *valence* expressed in such units. As such unit or standard the valence of hydrogen has been selected.

Further, if we compare the corresponding combinations of one and the same multivalent atom (that is to say, combinations in all of which the atom considered exerts the same atom-fixing power or *valence*) with other atoms of any other valence, we acquaint ourselves with the quantities of these last atoms which, among each other, possess equal chemical atom-fixing powers and are, therefore, equivalent. Thus, the following compounds of the metal cadmium are known :

$\text{CdO}$	$\text{CdS}$	$\text{CdCl}_2$	$\text{CdBr}_2$	$\text{CdI}_2$
Cadmium oxide.	Cadmium sulphide.	Cadmium chloride.	Cadmium bromide.	Cadmium iodide.

In all of these compounds cadmium appears with the same valence ; each compound may be converted into the other by double decomposition ; they correspond to one another perfectly ; hence, we conclude that the quantities of oxygen, sulphur, chlorine, bromine and iodine expressed by the symbols O, S,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , all have the same chemical atom-fixing power, or are equivalent. Moreover, it follows that one atom of oxygen or of sulphur is always equivalent to two atoms of chlorine, bromine, or iodine ; also, that if the last-mentioned elements must be regarded as univalent, which is in reality the

case,\* then must oxygen and sulphur be considered as bivalent.†

Very often a multivalent atom enters into combination with fewer other atoms than it is capable of binding, and this combination of atoms can then bind as many more atoms as may be necessary to saturate the full valence of the original multivalent atom. The former sort of compound is called unsaturated, in contradistinction from the latter so-called saturated compound. In this sense one atom of carbon (which is quadrivalent) combines with one atom of oxygen to form the gas carbon monoxide

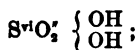
\* See note, page 41.

† The statements in the text are not to be considered final. If we were to consider only the above compounds of cadmium in connection with the data there given, the conclusions of the text would be all that could be attained, and it would follow that an atom of S or of O is always equivalent to two atoms of Cl, etc. But in reality, it is found that an atom of S can, and does, bind four atoms of Cl, which would make it not bivalent but quadrivalent, unless, indeed, SCl<sub>2</sub> be regarded as a case of "molecular addition" (SCl<sub>2</sub> + Cl<sub>2</sub>), against which view the weight of argument seems to militate; another even more convincing instance of the quadrivalence of S is furnished by the compound :



(Oefele, Ann. Chem. Pharm., Bd. 132, 1864, S. 82.)

In sulphuric acid, S is considered by most chemists as sexivalent:



nevertheless, not a few chemists, who still regard S as bivalent, write for sulphuric acid: HO.S.O.O.H.

The whole question as to the variability of the valence of the elementary atom is one of the most important questions bearing upon the science, and perhaps one may look for further fruitful investigation respecting this subject in the direction of thermo-chemistry,

[carbonous oxide],  $(C^{iv}O)^{+}$ , in which only two of the valences of the carbon atom are brought into activity.\*

But this gas is itself combustible; that is to say, is an unsaturated compound, and may unite with still another atom of oxygen, producing thereby carbonic anhydride  $(C^{iv}O)^{+}O^{+}$ , which is, on the other hand, a saturated compound. The relations are similar between stannous chloride,  $Sn^{iv}Cl_2$ ,† and stannic chloride,  $Sn^{iv}Cl_4$ , and there are many other like instances.

Such cases possess still a special interest for us, since they render evident what we are to understand by a radical or atom-group. One molecule of carbon monoxide unites with one atom of oxygen, producing one molecule of carbon dioxide [carbonic anhydride], which represents a saturated compound. Concerning the construction of the molecule of carbonic anhydride we can have the following two conceptions: a simple combination of one atom of carbon with two of oxygen, of which oxygen atoms each

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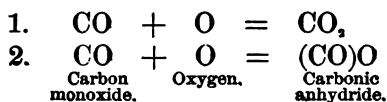
\* The view sometimes urged that the two remaining valence units of the C atom are active in saturating each other is incapable of extension to such compounds as NO and  $NO_2$ , if N be of uneven valence.

† It has been shown, quite recently, (V. and C. Meyer, Deutsch. Chem. Ges. Ber. XII, 1195) that the proper molecular weight for stannous chloride is double that which has been hitherto ordinarily written. Nevertheless, its correct molecular formula,  $Sn_2Cl_4$ , still represents an unsaturated compound, the two tin atoms being connected by double valences, as in the case of ferrous chloride (see p. 6):





exerts exactly the same chemical activity; or a combination of the original unsaturated compound, carbon monoxide, as a whole by itself, with one atom of oxygen, which latter oxygen atom will then possess another chemical function different from that of the oxygen atom originally in the carbon monoxide. By formulas these two views may be expressed as follows:



The idea of the atom-group, or radical, will become still clearer by a consideration of the compound, ammonium chloride, or of the ammonium compounds in general. By analysis we know that one molecule of ammonium chloride contains one atom of nitrogen, four atoms of hydrogen, and one atom of chlorine. This compound is quite similar to potassium chloride, the molecule of which consists of one atom of chlorine and one atom of potassium. In both molecules the chlorine atom may be replaced by an atom of bromine or of iodine, and in this manner we obtain from the ammonium chloride a compound of one atom of nitrogen, four atoms of hydrogen and one atom of bromine or iodine; from the potassium chloride, on the other hand, a combination of one atom of potassium with one atom of bromine or iodine. In other words: while in the one series of compounds the atom of potassium remains and is combined now with chlorine, now with bromine or iodine, in the other series of compounds the nitrogen atom and the

four hydrogen atoms are the components which we meet in all three substances :

(NH<sub>4</sub>) Cl  
Ammonium chloride.

KCl  
Potassium chloride.

(NH<sub>4</sub>) Br  
Ammonium bromide.

KBr  
Potassium bromide.

(NH<sub>4</sub>) I  
Ammonium iodide.

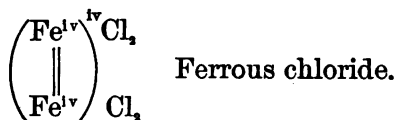
KI  
Potassium iodide.

We assume, therefore, that the nitrogen atom and the four hydrogen atoms constitute an atom-group which, as a whole, is in a condition to play the same rôle, can exert the same chemical function in combinations, as that of an elementary, simple atom. The principle of this consists in that such a radical\* is always an unsaturated compound and owes its origin to the circumstance that the valence units of a multivalent atom have been only partially saturated by other atoms; the valence units still remaining free determine then the valence of the radical thus formed. Nitrogen is, for example, a quinquivalent element; that is to say, a nitrogen atom is capable of binding five other univalent atoms; if it unites with four hydrogen atoms, there then remains one free valence unit which, in ammonium chloride, is satisfied or saturated by the chlorine atom just as the single valence of the potassium atom is satisfied in the compound potassium

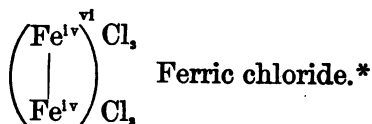
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\* The term "rest" is widely used to denote the same thing, a term formerly employed by Gerhardt. All compound "rests" are unsaturated molecules; but while many of the latter are known to exist in the free state, this can be said of but few so-called "rests." Single elementary atoms may be regarded as simple "rests."

chloride. Sometimes two or more atoms of the same element combine with one another, forming a double atom (radical) which naturally gives rise to a series of combinations different from that of the single atom, and is of a different valence from that of the single atom. Iron, Fe, is quadrivalent; in ferrous chloride two atoms of  $\text{Fe}^{\text{iv}}$  are connected with each other by two of the valences of each atom, while the remaining four valences are saturated by chlorine:



In ferric chloride, on the contrary, the two iron atoms are bound together by only one valence of each atom, and the remaining six valences are saturated by chlorine:



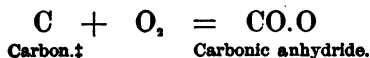
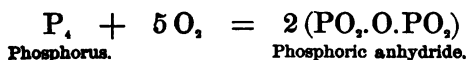
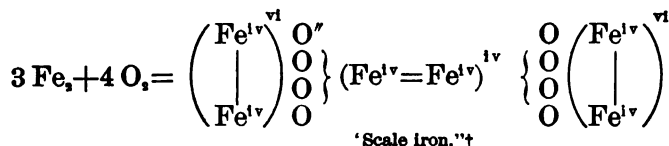
The fact that the free valences of a radical can be saturated by other radicals instead of by elementary atoms scarcely needs any special explanation; in this way we attain to molecules of constantly increasing complexity, in which the department of organic chemistry is so especially rich, and we find at the same time that the number of atoms which can combine to a single molecule is, *a priori*, unlimited.

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\* See note, page 5.

## OXIDATION AND REDUCTION.

By oxidation is understood, primarily, the combination of any substance with oxygen; by reduction, the reverse process, the abstraction of oxygen from a compound. Iron subjected to the action of moist air rusts by assimilating oxygen from the air;\* likewise, "scale oxide" is formed upon iron by oxidation when it is brought glowing into contact with air. In both cases a combination of iron with oxygen, an oxide, is generated, which covers the metal with a film. Phosphorus burns in air, by which process it combines with the oxygen of the air to form phosphoric anhydride; carbon oxidizes under similar circumstances to carbonic anhydride:



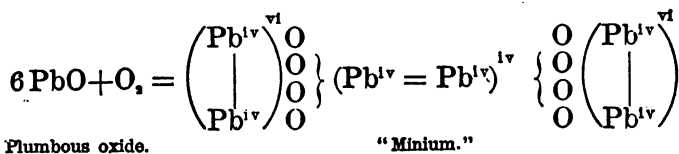
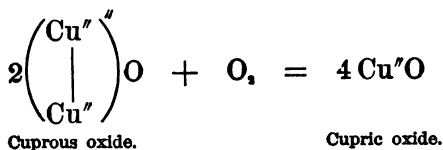
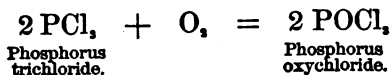
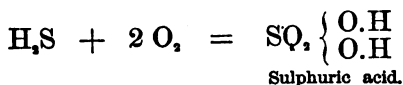
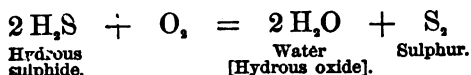
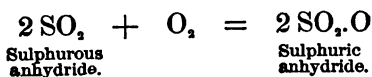
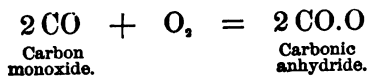

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\* Calvert has shown (Chem. News, xxiii, 98) that ordinary rusting of iron is largely due to the carbonic anhydride of the atmosphere.

† "Scale iron" appears to consist of two layers, the outer one of which contains a larger amount of ferric oxide than the inner one, but in varying proportions. The inner layer has had the formula  $6 \text{ FeO} \cdot \text{Fe}_2\text{O}_3$  assigned to it. (Mosander, Pogg. Ann. vi. 35.)

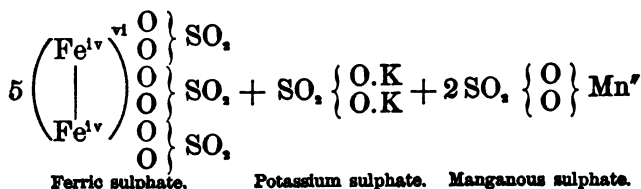
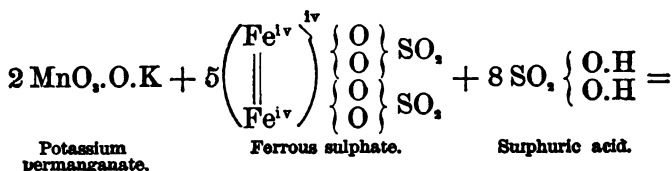
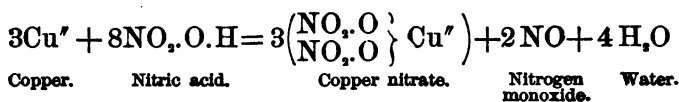
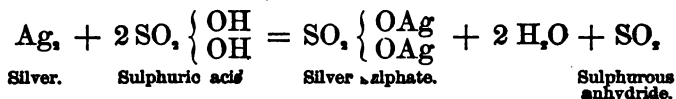
‡ We do not know how many atoms of carbon are contained in its molecule.

Compounds may oxidize still further, just as the elements in the above illustrations oxidized:

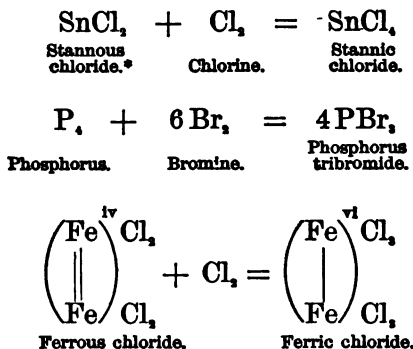


The oxygen necessary to accomplish the oxidation of a substance, however, may be obtained from a compound already containing oxygen, this latter

compound thereby suffering reduction. Such substances which easily give at least a portion of their oxygen to other substances are called oxidizing agents. Evidently, every substance is, with respect to every other substance which is capable of abstracting oxygen from it, an oxidizing agent, and inversely this oxygen abstracting substance is, with respect to the compound from which the oxygen is taken, a reducing agent. In this sense the following reactions ensue :



In these cases it was oxygen which effected the oxidation. Instances occur wherein chlorine or bromine work analogously :



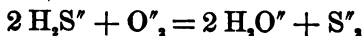
These reactions are plainly quite similar to the oxidation processes cited above; the oxides, chlorides, bromides, etc., produced correspond to one another perfectly with regard to their composition, and may easily be converted into one another.

The chemical processes which lie at the foundation of the examples just presented are not always of precisely the same kind ; rather must we distinguish cases where, through such oxidation, a change in the valence of the oxidized atom occurs from those in which mere substitution in consequence of double decomposition results. The oxidation of hydrous sulphide takes place in two different senses and is naturally attended by quite different results. The first equation shows that the hydrogen of the

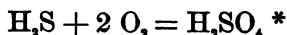
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\* See note, page 12.

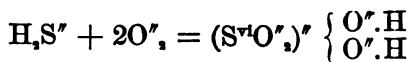
hydrogen sulphide is oxidized to water by the oxygen, and that sulphur is separated:



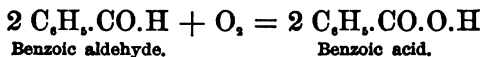
This reaction consists simply in the substitution of the bivalent sulphur by the bivalent oxygen; the hydrogen remains univalent as at first. The matter is different in the case of the formation of sulphuric acid from the same materials:



In this case bivalent sulphur changes to sexivalent sulphur, all of the valences of which are saturated by oxygen, at the same time the direct combination between the sulphur atom and the hydrogen atoms is sundered and is indirectly restored by the mediation of the two oxygen atoms. The mechanism of the process so described may be represented by the following equation:



This latter modality of oxidation, the insertion of an oxygen atom, occurs very frequently in the oxidation of organic compounds. Upon this method depends the oxidation of aldehydes to acids:

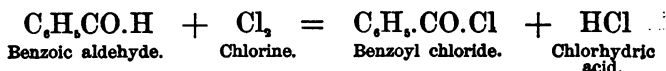



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\* See note, page 11.



The difference of this sort of oxidation becomes more apparent when we effect the oxidation by a univalent atom, as chlorine. In the case of oxidation with increase of valence [or in such cases as are represented by the last equation, where no such increase of valence occurs] the oxidizing atoms are simply incorporated, nothing being set free from the molecule, hence the molecule contains more atoms after the completion of the oxidation than before (see the examples cited above). If, on the contrary, chlorine acts upon benzoic aldehyde, chlorhydric acid is separated and the benzoyl chloride produced contains exactly the same number of atoms as the benzoic aldehyde:



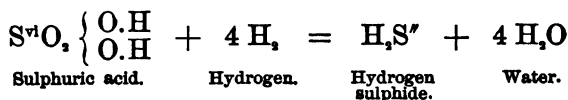
[this latter reaction being a case of substitution by double decomposition].

The preceding illustrations are sufficient to show that the term oxidation denotes processes differing much among themselves.\*

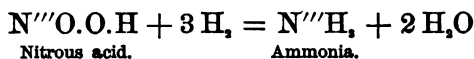
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\* With us it has been customary to regard *oxidation* and *reduction* as terms signifying processes the reverse of each other, and yet we very generally attach a much more extended meaning to the word *reduction* than to *oxidation*. We speak of *reducing* an oxide, sulphide or chloride, when oxygen, sulphur, chlorine, etc., are abstracted from these compounds respectively, while we restrict the application of the term *oxidation* to cases wherein oxygen is supplied to a compound, or some element is abstracted from it by oxygen. It will be seen that the author, throughout this work, has extended our custom-

The same is evidently true of the reduction processes; in many cases a lowering of the valence is entailed, as in the reduction of sulphuric acid to hydrogen sulphide:



In many instances, however, such is not the result, as in the reduction of nitrous acid to ammonia:



In this latter case the valence of the nitrogen atom is unchanged.

## SOLUTION OF THE METALS AND METALLIC OXIDES.

Most of the reactions which serve to distinguish and to separate substances from one another in the

any use of the term *oxidation* to correspond, in an opposite sense, to our application of the term *reduction*. In the stricter sense of the word *oxidation*  $\text{Fe}_2\text{Cl}_6$  would be an oxidation product when formed from  $\text{Fe}_2\text{Cl}_4$  by oxygen, thus:  $6 \text{Fe}_2\text{Cl}_4 + 3 \text{O}_2 = 2 \text{Fe}_2\text{O}_3 + 4 \text{Fe}_2\text{Cl}_6$ ; but if it be formed by simple addition of chlorine, as when  $\text{Fe}_2\text{Cl}_4$  is heated in chlorine gas, which may be represented by the equation of the text,  $\text{Fe}_2\text{Cl}_4 + \text{Cl}_2 = \text{Fe}_2\text{Cl}_6$ , the  $\text{Fe}_2\text{Cl}_6$  would be called a higher chlorinated product.

course of analysis can be effected only in solution; it is necessary, therefore, before we can test for a metal by these reactions, to bring it into solution. This solution, however, does not complete itself in the simple manner of the solution of a salt in water, but entails first the formation of some chemical compound of the metal and then the solution of this compound in the surrounding liquid. From what has been stated about oxidation, in the foregoing section, it is sufficiently apparent that it is chiefly an oxidation process which is concerned in the solution of a metal. The different methods by which we may bring about such have been already described, in general, and it only remains to elucidate somewhat more fully the prevailing behavior of the metals in particular. We shall then pass to a closer consideration of the action of the principal solvents. The simplest kind of oxidation is evidently that whereby the metallic atom unites directly with the oxygen atom. Many metals do this even at the ordinary temperature when they lie exposed to the air, especially if the air be moist. The polished surface of the metal loses its luster and becomes coated with a film of oxide or of a hydroxide which often abstracts carbonic anhydride from the atmosphere and becomes converted into a basic carbonate. Of the more commonly occurring metals, which alone enter into our discussion, iron, lead, copper, zinc, and arsenic are the ones which become most easily covered with a film of oxide upon exposure to the air. Indeed, iron, in a finely divided state such as that resulting from a reduction of

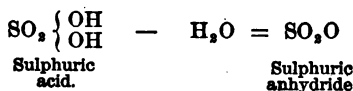
ferric oxide by hydrogen, is pyrophorous, taking fire at once in the air, and, glowing, burns to ferric oxide. Far easier than at the ordinary temperature does such oxidation take place when the metal is heated in air, or better, in pure oxygen. Under these conditions tin, antimony, cadmium, bismuth and mercury are oxidized, and the easier the higher the temperature (in the case of mercury, however, the oxide decomposes at a temperature but little higher than that at which it formed); also nickel and cobalt, in a dense state, oxidize at the temperature of incandescence; even silver when heated in the blowpipe flame to near its vaporization point gives a coating of silver oxide upon the charcoal. Only gold and platinum remain absolutely unattacked in the air. The combinations of metal with oxygen which are obtained in this way are called, in general, oxides. According as the oxides exhibit a lower or higher degree of saturation—that is, contain with reference to a fixed number of metallic atoms a smaller or greater number of oxygen atoms—they are distinguished by the terms *-ous* oxide, *-ic* oxide, sesquioxide, superoxide, bioxide [oftener and better dioxide, corresponding to monoxide], *-ous* anhydride, *-ic* anhydride, *per-ic* anhydride [or oxide], etc. The term *-ous-ic* oxide denotes a combination of two different oxides of the same metal. An absolutely definite meaning respecting the composition of oxides is generally attached, as a result of usage, only to the expression *sesqui-* and *bi-*oxide (instead of which the term *super-oxide* is often used); in the first case there occur three atoms of

oxygen to two of metal ; in the latter, two atoms of oxygen to one of metal.\*

The chemical characters of the metallic oxides differ widely and depend greatly upon the nature of the metallic atom itself. Generally speaking, however, so much may be said: the lower oxides are of a more basic, the higher ones of a more acid, nature. Hence, the intermediate oxides such as the sesquioxides are possessed of but feeble basic properties, the dioxides are indifferent compounds which, for the most part, do not combine with either bases or acids.†

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\* That is to say, such terms as *-ous* and *-ic* oxides are indicative of relative degrees of oxidation, an *-ic* oxide being a higher oxide than an *-ous* oxide. But metallic sesquioxide means two atoms of metal to three of oxygen ; with us, the terms metallic *dioxide*, *bioxide*, *super-oxide*, *hyperoxide* (especially the first two) generally denote two atoms of oxygen to one of metal, but can hardly be said to have as definite a meaning as the term sesquioxide. This latter has lately fallen somewhat into disuse as improved systems of naming have found more general adoption. In addition to our affixes *-ous*, *-ic*, our principal auxiliaries to terminology are the Greek prefixes *mon*, *di*, *tri*, etc., *hypo* and *hyper*, and the Latin prefixes *sub* and *super*. Certain oxides which may be regarded as derived from acids by the abstraction of  $H_2O$  are called *anhydrides*:



† In other words: the dioxides, or indifferent compounds of the metals with oxygen, do not tend to produce salts when treated to either acid or base. A basic oxide means one which tends to form a salt when treated to an acid or acid anhydride. Acid oxide is to be similarly understood in the opposite sense.

The following examples illustrate these principles:

**Manganese..**1)  $\text{MnO}$ , manganous oxide ; strongly basic.

2)  $\text{Mn}_2\text{O}_3$ , manganic oxide ; feebly basic.  
 $\text{Mn}_3\text{O}_4$ , manganous-manganic oxide.

3)  $\text{MnO}_2$ , manganese dioxide ; indifferent.

4)  $\text{MnO}_3$ , manganese trioxide [or manganic anhydride, corresponding to manganic acid :  $\text{MnO}_3 \left\{ \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \right\}$  ] ; an acid oxide.

5)  $\text{Mn}_2\text{O}_7$ , permanganic anhydride [from permanganic acid :  $\text{Mn}_2\text{O}_7 \cdot \text{OH}$  ] ; an acid oxide.

**Iron.....**1)  $\text{FeO}$  [or,  $\text{Fe}_2\text{O}_3$ ], ferrous oxide ; strongly basic.

2)  $\text{Fe}_2\text{O}_3$ , ferric oxide (sesquioxide) ; feebly basic.

$\text{Fe}_3\text{O}_4$ , ferrous-ferric oxide.

3)  $\text{FeO}_3$ , iron trioxide [or, ferric anhydride, corresponding to the acid  $\text{FeO}_3 \left\{ \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \right\}$  ] ; an acid oxide.

**Lead.....**1)  $\text{PbO}$ , plumbous oxide ; strongly basic.

2)  $\text{PbO}_2$ , lead hyperoxide [or lead dioxide, or plumbic oxide] ; indifferent.

3)  $\text{Pb}_3\text{O}_4$ , diplumbous-plumbic oxide ("minium").

Copper.....1)  $\text{Cu}_2\text{O}$ , cuprous oxide [suboxide];  
basic.

2)  $\text{CuO}$ , cupric oxide; basic.

Arsenic.....1)  $\text{As}_2\text{O}_3$ ,\* arsenious oxide [or arsenious  
anhydride, corresponding to the

acid  $\text{As} \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \end{cases}$ . (or the acid,  
 $\text{AsO.OH.})$ ];† feebly acid.

2)  $\text{As}_2\text{O}_5$ , arsenic oxide [or arsenic an-  
hydride, corresponding to the acid

$\text{AsO} \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} \quad \text{]};$  strongly acid.

In a manner similar to that in which the metals unite with oxygen they unite also with sulphur and the haloids, *i.e.*, chlorine, bromine, iodine, and fluorine. The compounds with these elements, especially those with sulphur, are analogous to the oxides, although they seldom manifest so decided a chemical character as the corresponding oxides. Moreover, these classes of compounds admit of being converted easily into oxides, and *vice versa*.

Sulphur, the atom of which like that of oxygen is

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\* The formulas for arsenious and antimonous anhydrides have been hitherto universally written as in this text:  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ . It has lately been shown that these are not justifiable expressions of the molecular weights of these substances, but that the formulas corresponding to the vapor density as determined by Mitscherlich some forty-five years ago (for arsenious anhydride) are correct, and that they should be written:  $\text{As}_4\text{O}_6$  and  $\text{Sb}_4\text{O}_6$ . (V. & C. Meyer, Deutsch. Chem. Ges. Ber. XII, 1112 and 1282.)

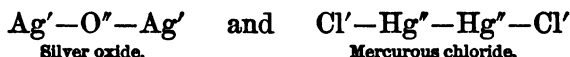
† See note, page 98.





of direct combination, the sulphides are also obtained by double decomposition, a process to which we resort in qualitative analysis in order to obtain them.

Chlorine attacks the metals even more energetically than sulphur, and, in some cases, than oxygen. Of the metals, with which we are here concerned, there is not one but will, upon the application of heat, combine directly with chlorine. The chlorine atom is univalent,\* and consequently can saturate only one valence of a metallic atom; therefore, it is incapable of uniting two metallic atoms in a molecule as oxygen or sulphur can do, so that in those molecules of chlorides which contain two atoms of metal these latter must be regarded as being directly united with each other. Silver oxide consists of two atoms of silver and one atom of oxygen which is bound to the two metallic atoms. Mercurous chloride contains two atoms of mercury and two atoms of chlorine, each of which chlorine atoms is to be considered as linked to an atom of mercury, while the mercury atoms are further bound to each other:



The combinations of chlorine with metals are also named *-ous* and *-ic* chlorides, etc. Their number is not so large as that of the oxides, since, as it appears, those corresponding to the higher oxides are incapable of existence. While most of the oxides and sulphides are insoluble in water, the reverse is

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\* Toward metals.

true of the chlorides: most of them dissolve in water. These solutions display the same chemical behavior as that of the solutions of the oxides in water, or correspondingly in oxygen acids. From this we conclude that in both cases the metallic atom possesses the same function, exerts the same chemical activity. In a great majority of cases, therefore, it is quite immaterial, for the application of chemical reactions, whether we bring the metal into solution as an oxygen compound or as combined with chlorine.

Bromine and iodine comport themselves toward the metals very much like chlorine, only they manifest a very considerably weaker affinity for them than chlorine possesses; both are also univalent.\*

It has already been stated that the oxidation of the metals can be accomplished otherwise than by direct union of the elements, namely, by subjecting them to the action of oxidizing agents, compounds which yield readily at least a portion of their oxygen. Strictly speaking, such compounds also belong here which are capable of readily giving up their chlorine, sulphur, etc., since the metallic compounds thus produced correspond to certain oxides respecting their grade of saturation.† By the oxidizing process which the metal undergoes, the oxidizing agents themselves become reduced; their number is naturally very large, but those which are ordinarily employed for the solution of the metals, and with which we have here to deal exclusively, are but few. They are the following: 1st, nitric acid; 2d, chlorhydric

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\* Toward metals.

† See note, p. 21.

acid, or dilute sulphuric acid; 3d, *aqua regia*;  
4th, concentrated sulphuric acid.

### 1) ACTION OF NITRIC ACID.

Nitric Acid is a combination of the univalent radical (atom-group)  $\text{NO}_2$ ,—which is itself a combination of a quinquivalent nitrogen atom with two bivalent oxygen atoms,—with one bivalent oxygen atom, the other valence of which is saturated by one univalent hydrogen atom (it is customary to consider this combination of an oxygen atom with one hydrogen atom as a special univalent radical,  $\text{OH}$ , and to call it *hydroxyl*), thus:  $(\text{N}^{\text{V}}\text{O}_2)^{\text{I}}\text{O}^{\text{II}}\text{H}$ . If the hydrogen atom in the hydroxyl be replaced by a metallic atom, a salt, a *nitrate*, as it is called, is produced. These salts are distinguished for their solubility in water; only a few basic salts are insoluble.\* The solubility of most of them diminishes significantly as the amount of nitric acid in the liquid increases, and many are completely insoluble in nitric acid itself, for instance the lead salt. Herein lies the explanation of the fact that many metals do not dissolve in the concentrated acid, in the pure compound, or do not even appear to be attacked by it at all. Action does really take place upon the surface of the metal in contact with the acid, but since the salt there formed is insoluble in the surrounding liquid it prevents further contact of metal and acid, and the action ceases. Hence, for the solution of the metals a too concentrated acid should

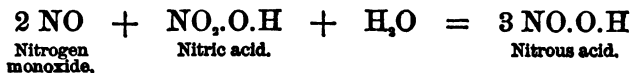
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\* See note to p. 38.

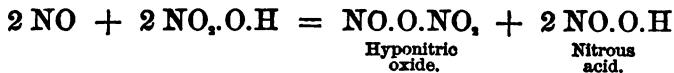
not be employed, but one of moderate strength. The action of metals upon nitric acid commences in many cases at a low temperature and with quite dilute acid (copper, zinc); it is greatly accelerated by the agency of heat as well as by the presence of nitrous acid in the nitric acid, so that the action is much more energetic with deeply colored acid than with the colorless. Moderately concentrated nitric acid (that is, not too dilute) is always reduced by the metals to nitrogen monoxide, yielding three atoms of oxygen :



If the acid be rather dilute the nitrogen monoxide is completely or partially evolved, but if the acid be of stronger concentration it will be absorbed by the nitric acid, producing nitrous acid; or, in case of still stronger concentration, producing hyponitric oxide. In these instances the following reactions occur :

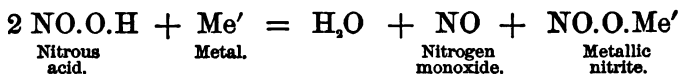


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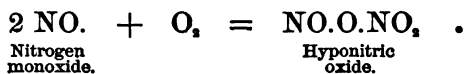


The nitrous acid is very easily decomposed by metals, with the formation of nitrogen monoxide and nitrite

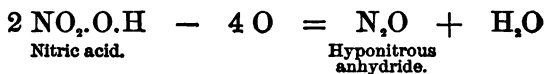
salts, which latter, however, are immediately decomposed by the nitric acid present :



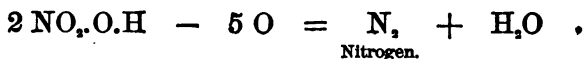
According to this, the nitrous acid is the real intervening instrumentality in the action between metals and nitric acid ; its quantity increases greatly in the course of the reaction. The nitrogen monoxide combines at once with oxygen, in contact with air, forming hyponitric oxide, which manifests itself as a reddish brown vapor :



Sometimes the reduction of the nitric acid goes still further than to nitrogen monoxide, when hyponitrous anhydride, or even nitrogen, is evolved :

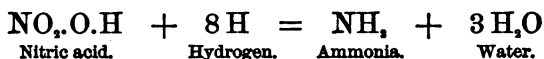


and



Zinc, with cold dilute acid, generates hyponitrous anhydride ; at a somewhat higher temperature, also nitrogen monoxide. Copper generates, in the cold, nitrogen monoxide with which, at higher temperatures and by stronger concentration, nitrogen is

mixed. Silver, mercury, bismuth, lead and antimony behave similarly. With very dilute nitric acid zinc gives ammonia; the same reaction occurs with somewhat stronger acid when free sulphuric acid or chlorhydric acid is present; if zinc be treated to dilute sulphuric acid the rapid evolution of hydrogen may be easily arrested by allowing nitric acid to drop into the generating flask; under this treatment a point is reached at which the metal dissolves in the liquid without the evolution of gas. The reaction occurs according to the following equation:

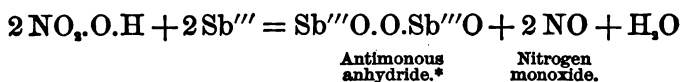


the hydrogen abstracts from the nitric acid all of its oxygen, and forms ammonia with the nitrogen. The same process is accomplished without the presence of any other acid when zinc is dissolved in very dilute nitric acid. We conclude, therefore, that very dilute nitric acid acts upon zinc just as chlorhydric acid or dilute sulphuric acid (see below), only the hydrogen is not evolved in the gaseous state, but is at once consumed in the formation of ammonia. Tin behaves like zinc.

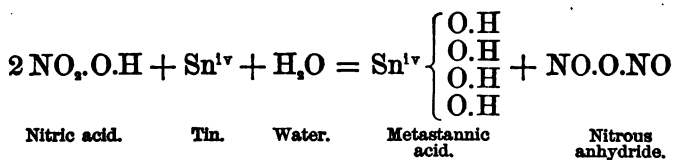
The reduction of nitric acid and its change into ammonia take place not only in acid, but also in neutral and alkaline, solutions. If a solution of neutral lead nitrate be boiled with metallic lead, a part of the nitric acid becomes reduced to nitrous acid, and double salts of lead nitrate and lead nitrite are formed. In alkaline solution nitric acid is con-

verted into ammonia by boiling with iron and zinc (since these two metals together, treated to a solution of potassium hydroxide, generate hydrogen).

The oxygen which the nitric acid gives off in the reactions hitherto considered is employed in the oxidation of the metal present ; thus, nitric acid and antimony give :



Tin comports itself similarly toward strong nitric acid, only there is formed not an anhydrous oxide but a hydroxide :

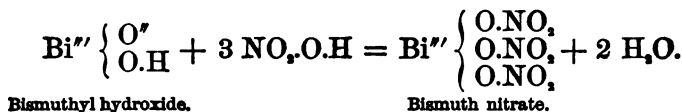
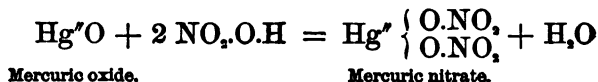
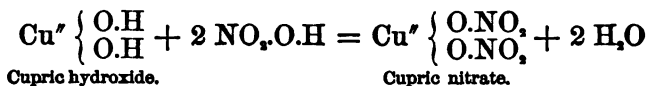
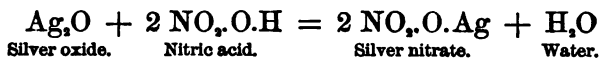


These two metallic oxides are insoluble in the excess of acid ; the oxides of the other metals which are oxidized by nitric acid are soluble in the excess of acid. From this we see that the process of the solution of a metal in nitric acid does not complete itself in one reaction, but rather in two successive stages. First, the metal is oxidized ; and, secondly, this oxide is dissolved in the acid, whereby are formed a

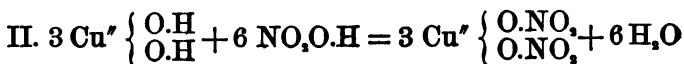
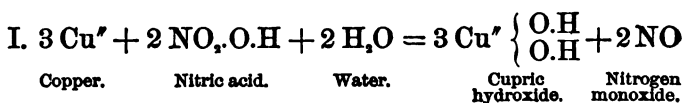
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\* See note, p. 27.

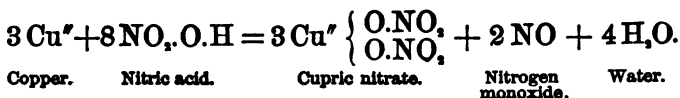
nitrate salt and water. The following equations elucidate such processes of solution :



The reactions which attend the solution of copper, for instance, in moderately concentrated nitric acid may be represented by the following equations :

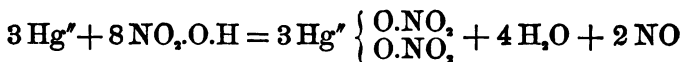


or :





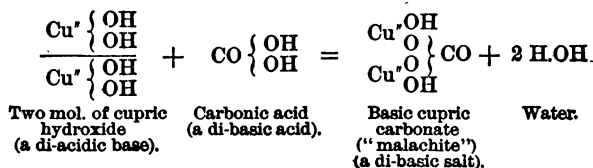
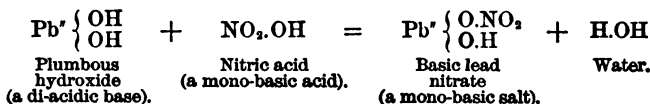
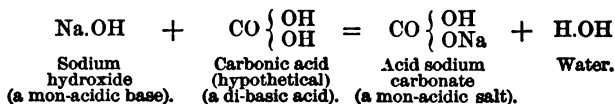
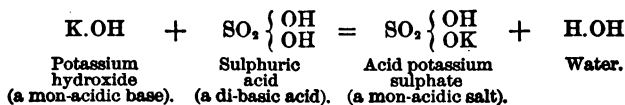


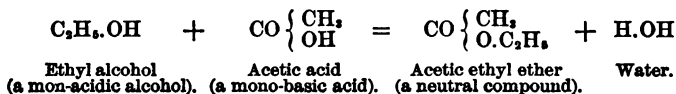
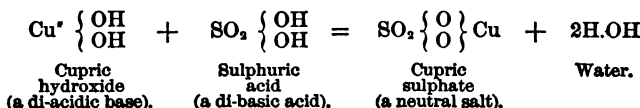
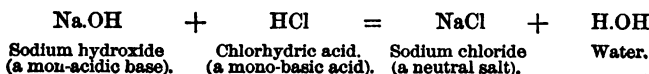
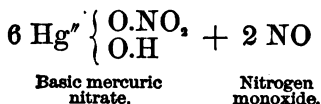
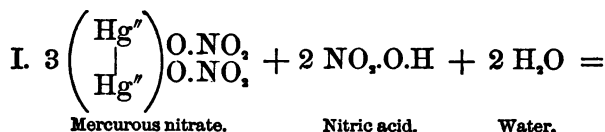


Mercury.      Nitric acid.      Mercuric nitrate.      Water.      Nitrogen monoxide.

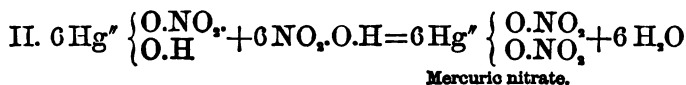
If we employ the mercurous nitrate we may consider that at first a basic mercuric nitrate is produced, which, in course of further action, is converted into a neutral salt: \*

\* Salts may be regarded as derived 1) from acids by substitution of part or all of their replaceable hydrogen by *basic rests*, and 2) from bases by similar displacement of their hydrogen by *acid rests*. When only a part of the replaceable hydrogen (replaceable in this sense) of an acid has been so replaced an *acid salt* results; when only a part of the corresponding hydrogen of a base has been thus replaced a *basic salt* results; when neither "basic" nor "acid" hydrogen is left in the salt, then the salt is *neutral*. To illustrate these considerations we may write:

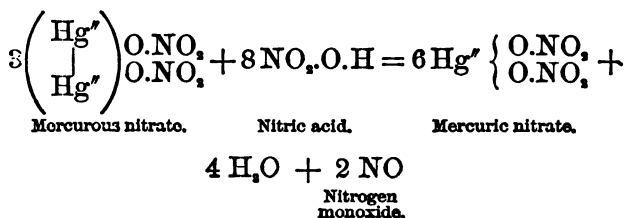




From the above equations it appears that a base is *mon-, di-, tri- . . . . . n-acidic* according as it contains one, two, three . . . . . *n* atoms of hydrogen replaceable, in the sense of these notes, by acid rests. Correspondingly, an acid is *mono-, di-, tri- . . . . . n-basic* according as it has one, two, three . . . . . *n* atoms of hydrogen replaceable by basic rests. Generally, in oxygen acids, this replaceable hydrogen is that of the OH (hydroxyl) group. But we have also hydracids like: HCl (mono-basic) and SH<sub>2</sub> (di-basic). It may be remarked that, in metallic salts, carbonic acid functionates as a di-basic acid, while in its ethers it appears also as tetra-basic: C(OH)<sub>4</sub>.

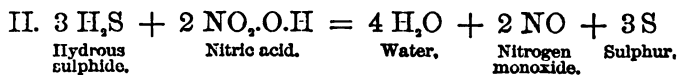
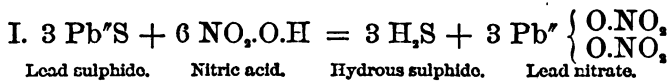


OR :

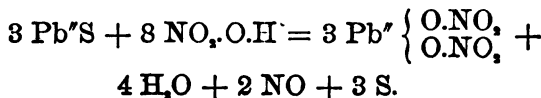


The other metals which form several oxidation products behave similarly, as iron, tin, antimony, arsenic; these are at first converted into the lower oxides by moderate action of nitric acid.

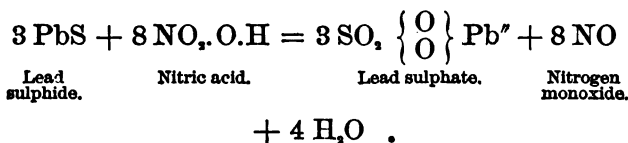
The metals and their lower oxides are not the only substances which we have to oxidize by nitric acid, in course of analysis; most of the metallic sulphides come into the same category. If the nitric acid employed be dilute, then the sulphur of the sulphide separates as such, while the metal passes into solution as nitrate :



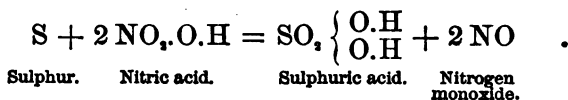
OR :



The hydrous sulphide which is formed at first is at once oxidized by the excess of acid present, a reaction which occurs incidentally when hydrous sulphide is conducted into cold, concentrated, or warm, diluted, nitric acid. By fully concentrated, especially red fuming, nitric acid the metallic sulphides are converted into sulphates without separation of sulphur :



Even free sulphur in a finely divided state becomes perfectly oxidized to sulphuric acid by prolonged heating with very concentrated nitric acid :

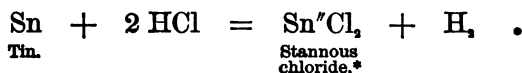
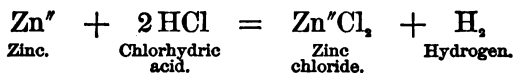


## 2) ACTION OF CHLORHYDRIC ACID AND OF DILUTE SULPHURIC ACID.

Chlorhydric acid [such as is kept in the bottles of the laboratory] is a solution of chlorhydric acid gas in water.\* Chlorine and hydrogen are both univalent,

\* J. Thomsen (Pogg. Ann. Jubelband, 1874, S. 135.) has regarded the aqueous solution of chlorhydric acid as  $\text{ClOH}_2 = \text{H}_2\text{Cl} - \text{OH}$ . This conception assumes a multivalence for the chlorine atom, even respecting hydrogen. Chlorine is regarded by some writers as multivalent with respect to more negative elements (see formulas for chloric acid, *etc.*, page 130.

and therefore can unite with each other in only one proportion, that of one atom of each ; the resulting chlorhydric acid is a colorless gas, which dissolves in large quantities and with great avidity in water, forming a colorless and, when concentrated, somewhat strongly fuming solution in contact with the air. Chlorhydric acid works upon the metals much less energetically than nitric acid ; only iron and zinc dissolve in it easily ; tin, cadmium, cobalt and nickel are respectively less and less soluble in it, and the metals lead, copper, bismuth, antimony, arsenic, mercury, silver, gold and platinum are either altogether insoluble or only traces of them dissolve. In all cases of solution the metal dissolves with simultaneous evolution of hydrogen ; the chlorhydric acid is decomposed, whereby the metal takes the place of the hydrogen, forming a metallic chloride :

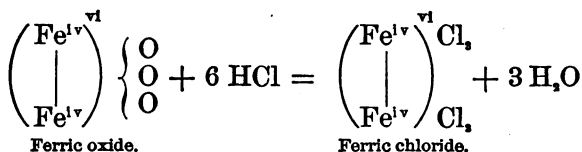
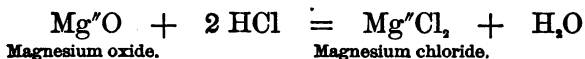
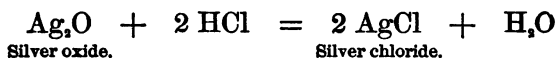


It is noteworthy that in all such instances only the lower chlorides are formed, even when hot concentrated acid is employed, since these lower chlorides are not capable of decomposing the chlorhydric acid.

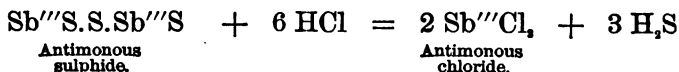
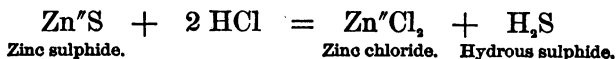
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\* See note, page 12.

The metallic oxides are mostly very easily decomposed by chlorhydric acid, producing by double decomposition a metallic chloride and water :



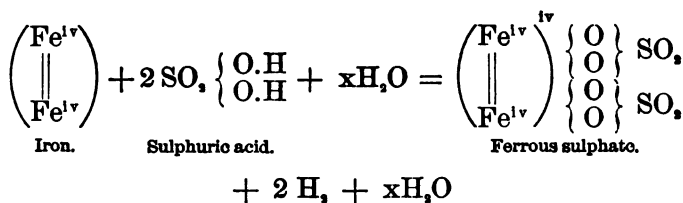
Metallic sulphides give, by similar treatment, metallic chloride and hydrogen sulphide :



Many sulphides, however, which when treated to hot concentrated chlorhydric acid are dissolved with evolution of hydrogen sulphide, are not attacked at all by the cold, dilute acid.

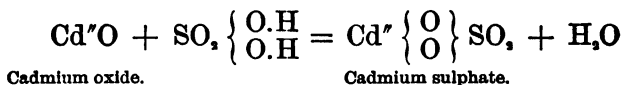
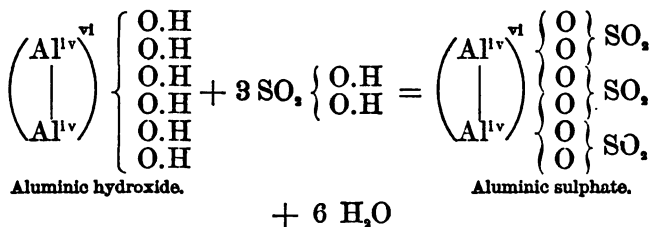
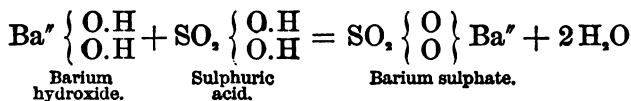
Quite similar to the action of chlorhydric acid upon metals is that of dilute sulphuric acid. The metals

cited above as soluble in chlorhydric acid dissolve also in dilute sulphuric acid with evolution of hydrogen and the formation of metallic sulphates :

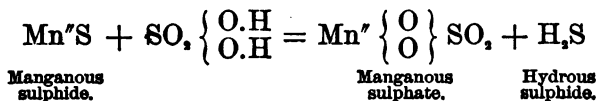


(the term  $x\text{H}_2\text{O}$  is introduced into the equation merely to indicate dilution of the acid).

The metallic oxides and some sulphides are changed into sulphates in a manner corresponding to the formation of chlorides effected by chlorhydric acid as given above :

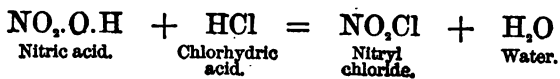






### 3) ACTION OF AQUA REGIA.

The name, aqua regia, designates a mixture of one part of nitric acid with from two to three parts of chlorhydric acid. It is distinguished by the very remarkable oxidizing energy with which it attacks metals; even gold and platinum are readily dissolved by it. The powerful oxidizing\* property of aqua regia is due to the quantity of free chlorine contained in it, which is liberated by the action of the nitric and chlorhydric acids upon each other. This reaction between the two acids consists in the formation of water from the hydroxyl group of the nitric acid and the hydrogen of the chlorhydric acid, while hyponitric oxide, nitrosyl chloride, nitryl chloride (?) and chlorine are also produced. According to the temperature and degree of concentration of the liquor the one or the other of the reactions expressed by the following equations appears to ensue:



(the  $\text{NO}_2.\text{Cl}$  is probably contained besides  $\text{NO}.\text{Cl}$  in the so-called chlor-hyponitric acid),

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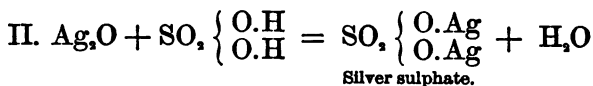
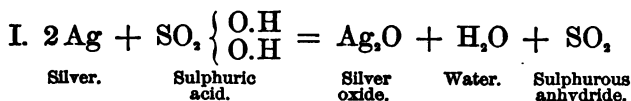
\* See note, page 21.



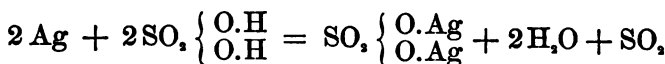
These reactions begin at the ordinary temperature and continue until a certain quantity of the decomposition products quoted have been formed; in consequence the fluid assumes a yellow color. If the new products are removed by heat or by the insertion of a metal into the fluid which combines with the free chlorine and also abstracts the chlorine from the nitrosyl chloride, the reaction between the nitric acid and chlorhydric acid is renewed until, finally, one of the two acids is exhausted. Generally the chlorhydric acid is present in excess, in consequence of which, upon evaporation of the aqua regia solution of a metal, the latter is obtained in combination with chlorine as a metallic chloride. The decomposition products of the nitric acid, principally hyponitric oxide, nitrogen monoxide, and nitrous anhydride, are set free with effervescence, as gases. Accordingly, it is readily comprehensible why a nitrate may be so easily changed to the corresponding chloride by evaporation with excess of chlorhydric acid; the nitric acid is decomposed entirely by a portion of the chlorhydric acid, and is evolved, while the base and remaining chlorhydric acid react upon each other, giving a metallic chloride and water. Inversely, metallic chlorides may be converted into metallic nitrates by evaporating with nitric acid.

## 4) ACTION OF CONCENTRATED SULPHURIC ACID.

Sulphuric acid is a combination of the bivalent radical  $\text{SO}_2$  (a combination of one atom of sexivalent sulphur with two atoms of bivalent oxygen) with two hydroxyl groups (see above, under nitric acid), thus:  $(\text{SO}_2)'' \left\{ \begin{smallmatrix} \text{O.H} \\ \text{O.H} \end{smallmatrix} \right. *$  It is an oily liquid, which evolves much heat when mixed with water. Under the agency of heat, especially upon boiling, many metals are converted into sulphates which are not attacked by dilute sulphuric acid; they are at first oxidized by a reduction of the sulphuric acid to sulphurous anhydride and water, and subsequently the oxide formed is converted into a metallic sulphate:



or:

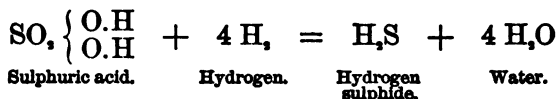


Copper, mercury and bismuth behave like silver; in the case of copper, however, some cupric sulphide is always formed.

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\* See note, page 11.

It should be remarked that, when zinc is treated to only slightly diluted sulphuric acid, a part of the sulphuric acid is reduced by the hydrogen in *statu nascendi* to hydrogen sulphide :



### MANNER IN WHICH THE REAGENTS WORK.

In the preceding section we have seen how we may bring a metal into solution, how we may cause it to combine with other bodies, and now the question would naturally arise whether it be possible or not to determine what metal is in solution without again separating it in the metallic state. The answer to this question is obvious from the fact that no two metals in solution behave exactly alike; the solutions of the different metals manifest different reactions. The distinctions in this respect are often only slight, and not at all striking; sometimes, however, they are very significant. Copper and lead, for instance, are both precipitated from solution by hydrogen sulphide, possessing a brownish-black color; cadmium, on the contrary, falls yellow; moreover, the reaction may not take place in very dilute solutions, or it

may occur even when the merest traces of the substance are in solution. Calcium solutions give a precipitate with sulphuric acid only when they are not too dilute, while solutions of barium, even when extremely dilute, yield evidence of its presence by the employment of the same reagent. It is further noteworthy that the metals, according to their behavior with respect to certain reagents, admit of a classification into groups, the individual members of which exhibit more or less of similarity in their deportment; thus, many metals are precipitated from acid solutions by hydrous sulphide (copper, lead, and others), while many others are not (iron, zinc). This principle is most advantageously applied in analysis by testing for the presence of whole groups and separating them, whereupon further research is conducted respecting their individual members.

Concerning the phenomena of a reaction, the following cases may be distinguished, in general :

- 1) *A precipitate is produced*, that is to say, upon bringing together two clear solutions, a solid (or liquid) substance separates, which is insoluble in the surrounding liquid. In this way calcium carbonate separates as a solid, insoluble substance when solutions of calcium chloride and sodium carbonate are mixed together, causing the clear liquid to become opaque. If we pour water into a solution of chloroform in alcohol, this liquor also becomes cloudy, but the substance precipitated, in this case, is not a solid, but consists of innumerable minute drops of chloroform. If the quantity of the precipitate produced be very slight the liquid only becomes

cloudy, and, in cases of mere traces of a precipitate, exhibits only a slight opalescence or a bluish tint (as in the case of silver chloride). The physical properties of the precipitates may display very distinctive characteristics, which should be noticed very carefully; some are flocculent and very voluminous, like aluminic hydroxide; others are almost transparent, quite gelatinous, and hence difficultly visible, like silicic acid; others are pulverulent without presenting a crystalline appearance, like lead sulphate; others, again, are manifestly crystalline, in which case they exhibit, when the light falls upon them, especially direct sunlight, a peculiar glistening caused by the reflection of the light from the mirror-like faces of the minute crystals, which may often be easily distinguished by means of a small magnifying lens; such a precipitate is the double ammonium-magnesium phosphate. Still others are at first amorphous, flocculent and voluminous, but become crystalline after a time and decrease in volume to an extraordinary degree: calcium carbonate furnishes an example of this kind of precipitates. Finally the solubility of the precipitates should be regarded; many are not absolutely insoluble in water, but only difficultly soluble, in consequence of which they are not produced in very dilute solutions, or if produced vanish again upon the addition of much water: lead chloride and calcium sulphate are illustrative of such. Many, on the contrary, are as good as insoluble in water, as barium sulphate; but dissolve upon the addition of an acid, as, for instance, calcium oxalate; or upon the addition of an alkali, as does arsenic trisulphide;

or upon the addition of ammonia—for instance, silver chloride. Many dissolve directly in an excess of the precipitant, as in the case of zinc hydroxide, which is precipitated from solutions of zinc by sodium hydroxide solution, and then dissolves in an excess of the latter.

2) *A change of color occurs*, including the cases where the fluids which are mixed in order to produce the reaction were colorless or colored, and become respectively colored or colorless, or change their colors. A solution of ferric chloride diluted so that it is colorless becomes red upon the addition of a colorless solution of potassium sulphocyanate; on the contrary, the red solution of permanganic acid is decolorized by oxalic acid; a green nickel solution is colored blue by ammonia; a red chromic acid solution becomes yellow by the action of ammonia, and green by the agency of alcohol. It is especially worthy of attention that, in cases where the liquor becomes very dark or quite opaque, one is inclined to judge that no precipitation has occurred; in such instances it is necessary to convince one's self of the transparency of the fluid by attentively regarding a thin film of it.

3) *Effervescence ensues*. This appearance occurs only when, in course of the reaction, a substance is separated which, at the temperature and pressure then obtaining, is gaseous and is not absorbed by the surrounding fluid. That much depends upon this last-mentioned condition may be illustrated from the fact that dilute sulphuric acid does not effervesce with sodium chloride, because the chlorhydric acid gas which is produced is readily absorbed

by the surrounding liquor ; but a strong effervescence ensues, that is to say, a brisk evolution of gas, when concentrated sulphuric acid is poured upon sodium chloride, because the chlorhydric acid gas is not absorbed by this strong acid.

Naturally, the manifestations cited above may occur simultaneously : two colorless solutions may produce a colored precipitate (silver arsenate) ; or evolve a colored gas (chlorine) ; or the fluid may change its color, while a colorless precipitate is formed (sulphur from chromic acid and hydrogen sulphide), etc.

Moreover, cases may occur in which a reaction is really completed without being accompanied by any of the signs just mentioned. In such instances there is often a noticeable change of temperature, as when soda lye is saturated with nitric acid ; but sometimes even this sign apparently fails, evidently because it is too slight to be perceived without more delicate means of detection, as when mercuric nitrate and sodium chloride are transformed into mercuric chloride and sodium nitrate.

These introductory remarks completed, we will now pass to a closer consideration of the mode of action of the individual, principal reagents. They are the following : 1, sulphydric acid ; 2, ammonium sulphide ; 3, potassium (or sodium) hydroxide solution ; 4, ammonia ; 5, sodium carbonate ; and 6, ammonium carbonate. These reagents are employed for the recognition of the bases ;\* for the determination of the acids there

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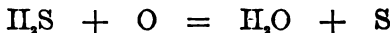
\* See note, page 69.



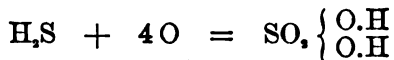
still remain : 7, barium chloride ; 8, lead acetate ; 9, silver nitrate.

1) *Sulphydric acid*,  $\text{H}_2\text{S}$ . [hydrogen sulphide, or hydrous sulphide.]

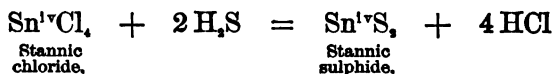
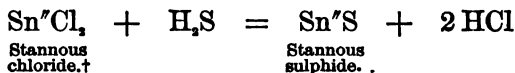
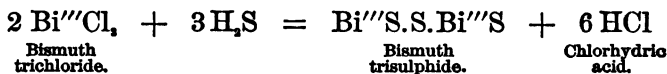
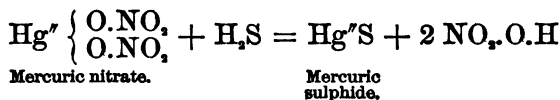
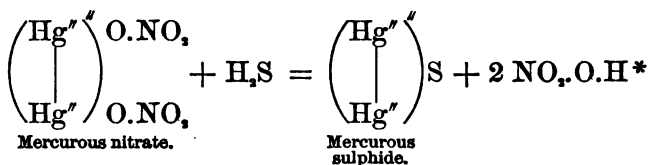
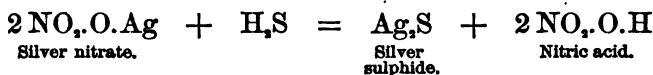
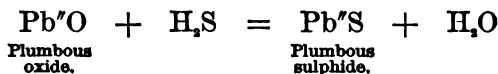
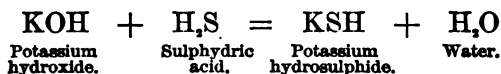
Sulphydric acid is a combination of one atom of bivalent sulphur with two atoms of hydrogen ; it is a colorless gas, possessing an odor akin to that of rotten eggs, and is absorbed in small quantities by water. This solution, sulphydric acid water, when in contact with the air, soon deposits sulphur, which is separated by the oxygen of the air with attendant formation of water :



A small portion of the sulphydric acid is also oxidized to sulphuric acid :



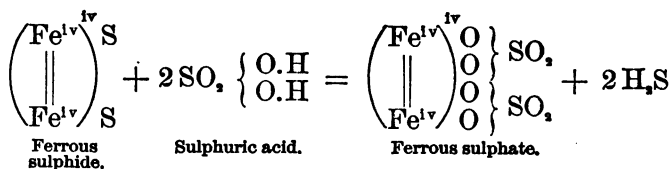
When sulphydric acid is brought into contact with metallic oxides or metallic salts a double metathesis usually results ; the oxygen which was combined with the metal unites with the hydrogen while the metal unites with the sulphur. In general, we may say that the hydrogen and metal change places, and the number of hydrogen atoms thus changing places always equals the sum of the active valences of the metallic atoms ; the following examples illustrate this :



\* It hardly need be remarked that the "active valences," in the sense of the text, are here those of the mercurous group, as a whole.

† See note, page 12.

Most of the metallic sulphides thus produced are insoluble in water (and are colored), hence they separate as precipitates when sulphydric acid is brought into solutions of such metals. In some instances they are soluble in acids by which they are decomposed, yielding a metallic salt and hydrous sulphide:



According to this deportment of their sulphides, the heavy metals admit of division into two great groups:

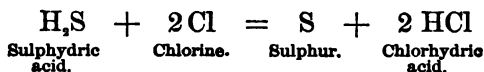
1) Those which are precipitated from acid solutions by sulphydric acid, and

2) Those which are not precipitated from acid solutions, but are precipitated from alkaline (incompletely from neutral) solutions.

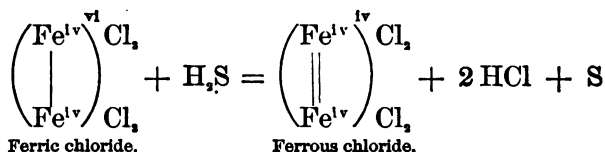
The metals which belong to the first group, however, are completely precipitated as metallic sulphides only when the solutions do not contain too much free acid, and especially when they are cold, since warm, strong chlorhydric acid and even dilute, warm nitric acid exert a strong solvent action; hence, when the above conditions are not fulfilled, the precipitation is not complete.

In many cases sulphydric acid works also as a reducing agent, when sulphur is always separated.

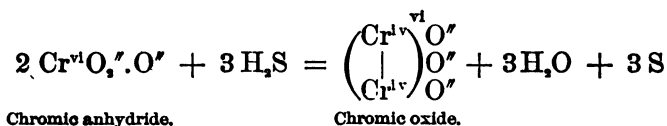
Similar to the action of free oxygen (see above) is that of free chlorine, bromine, and iodine; with separation of sulphur there is formed chlorhydric acid, etc.:



Ferric solutions, when acid, are reduced to ferrous solutions by sulphydic acid:



Chromic acid in acid and in alkaline solutions reduces to chromic oxide:

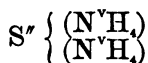


Arsenic acid in acid solution becomes reduced to arsenious acid; chloric acid, bromic acid, iodic acid, the acids of manganese and sulphurous acid are likewise reduced, also nitric acid (and hence it happens that a metal which is not precipitated from a chlorhydric acid solution may be completely pre-

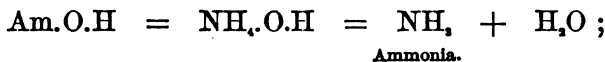
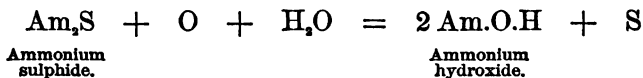
precipitated from a nitric acid solution, since the nitric acid is decomposed as soon as it is liberated).

2) *Ammonium sulphide*,  $(\text{NH}_4)_2\text{S}$ .

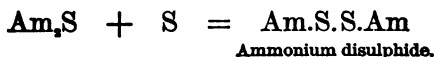
Ammonium sulphide is a combination of two atom-groups of ammonium (consisting of one atom of quinquivalent nitrogen combined with four atoms of hydrogen) with one atom of bivalent sulphur; accordingly, its formula is:



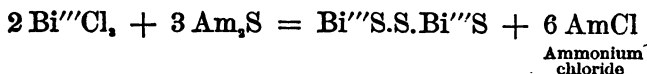
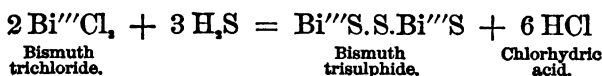
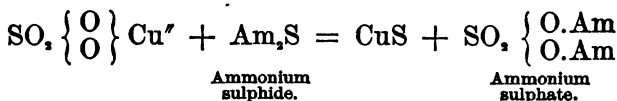
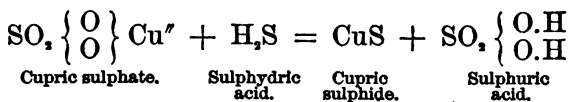
or, shorter:  $\text{Am}_2\text{S}$ , in which Am denotes the group or radical,  $\text{NH}_4$ . The solution of this compound, which is at first colorless, becomes gradually yellow in contact with air; the oxygen of the air separates a part of the sulphur from the ammonium with attendant formation of ammonium hydroxide, which, however, immediately decomposes into water and ammonia:



but the separated sulphur dissolves in the still undecomposed ammonium sulphide, forming a polysulphide:

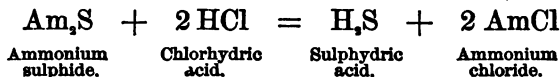


The action of ammonium sulphide is quite similar to that of sulphydric acid; like the latter, it gives rise to metallic sulphides upon being brought into contact with metallic compounds. While, however, by the action of sulphydric acid an acid is set free, one or more hydrogen atoms replacing the metallic atom of the salt, such is not the case when the precipitation is effected by ammonium sulphide, but there is formed an ammonium compound corresponding to the metallic compound employed, and the neutrality of the solution is maintained. The following equations illustrate this important distinction between the action of sulphydric acid and that of ammonium sulphide:



In consequence of this circumstance that the neutrality of the solution is undisturbed, ammonium sulphide precipitates those metals from neutral solutions completely which are precipitated by sulphydric acid only from alkaline liquors.

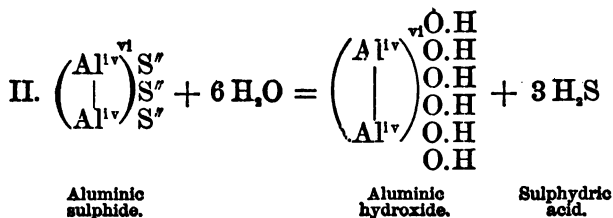
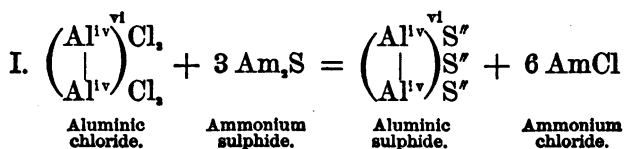
Ammonium sulphide is decomposed by acids just as the sulphides of those metals are which are not precipitated from acid solutions by sulphydric acid ; sulphydric acid is evolved and an ammonium compound is formed :



If, then, ammonium sulphide be added to an acid solution of a metal which is not precipitated by sulphydric acid, precipitation does not ensue until all of the free acid has been consumed in the decomposition of the ammonium sulphide, and the liquor has, in result of this, become neutral. For this reason an acid solution must be neutralized with ammonia or sodium carbonate before the addition of ammonium sulphide. It may be remarked, incidentally, that the metallic sulphides precipitated by sulphydric acid, or by ammonium sulphide, tend, for the most part, to oxidize readily in contact with air, especially when they are moist. Hereby are formed, analogously to the oxidation of sulphydric acid itself, partly metallic hydroxides with separation of sulphur, and partly metallic sulphates. Since the latter are mostly soluble in water, a loss

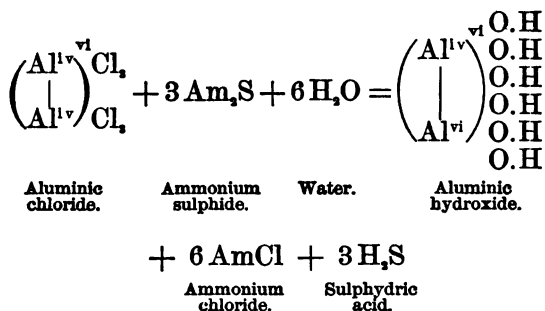
would be sustained upon washing such partially-oxidized precipitates with water ; such loss may be prevented by the addition of a small quantity of sulphydric acid or of ammonium sulphide to the wash-water.

In some instances ammonium sulphide acts under a guise different from that just considered, inasmuch as instead of a metallic sulphide the corresponding metallic hydroxide is precipitated. This is accounted for by the fact that the metallic sulphide *in statu nascendi* reacts at once with the elements of water, producing a metallic hydroxide and sulphydric acid, which latter compound either is evolved as a gas or remains absorbed in the fluid. The entire process is completed in two phases in accordance with the following equations :

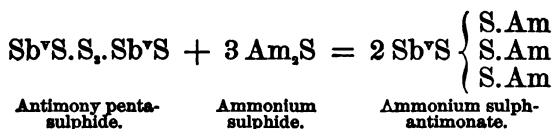


OR :





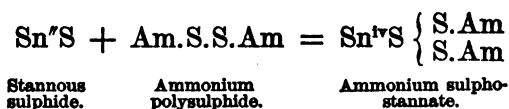
Ammonium sulphide suffers further employment in the separation of the metallic sulphides which are precipitated from acid solutions by sulphydic acid. It has been already stated that the sulphides, like the oxides, are partly of an acid, partly of a basic, and partly of an indifferent, nature; the first two of these classes of sulphides unite with each other, forming so-called sulpho salts,\* of which those with an alkaline base are soluble in water. In consequence of the formation of such salts, ammonium sulphide is capable of dissolving the sulphides of an acid nature (tin, arsenic, antimony, gold and platinum sulphides); with antimony pentasulphide there is formed the compound:




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\* See note, page 28.

If an acid be added to an aqueous solution of such a sulpho salt, the ammonium sulphide is decomposed, as already stated, and the acid sulphide separates out. If the ammonium sulphide possesses a yellow color, containing, therefore, ammonium polysulphide, the solution of the metallic sulphide may be accompanied by an oxidation;\* for instance, brown stannous sulphide does not dissolve in the colorless ammonium monosulphide, but easily in the yellow disulphide, forming stannic ammonium sulphide:



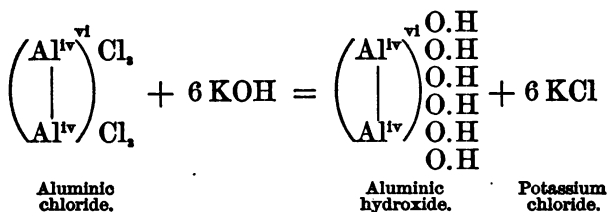
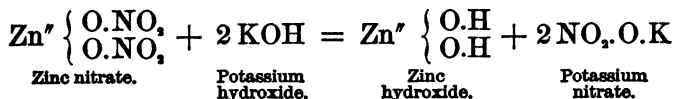
Finally, sodium sulphide and potassium sulphide are quite similar, in their action, to ammonium sulphide.

3) *Potassium (or sodium) hydroxide solution, KOH.*

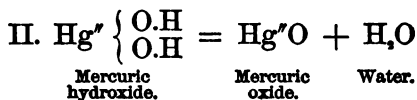
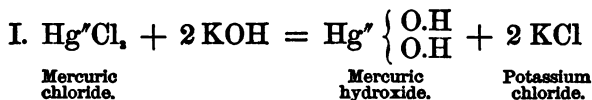
This name is given to the aqueous solution of a compound consisting of one atom of bivalent oxygen with one atom of potassium (or sodium) and one atom of hydrogen:  $\text{KO}^{\text{H}}$  (or,  $\text{NaO}^{\text{H}}$ ). Upon the addition of a solution of potassium hydroxide to metallic solutions a double metathesis obtains: the potassium and the other metal exchange places, and a precipitate of a metallic hydroxide is formed:

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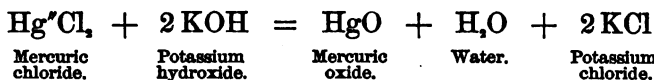
\* See note, page 21.



Sometimes, however, these metallic hydroxides decompose at once into water and a metallic oxide, which latter separates as such :



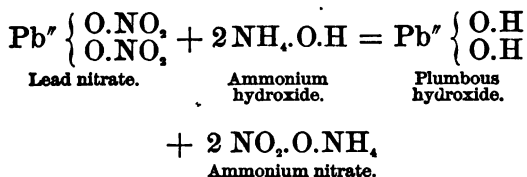
or :



Cupric hydroxide undergoes a similar decomposition only after some time has elapsed, or upon heating the liquor containing it. Many metallic hydroxides are soluble in potassium hydroxide solution, thus forming compounds of the nature of salts in which the metallic oxide plays the rôle of an acid anhydride; the case of potassium zincate is of this sort:  $\text{Zn}'' \left\{ \begin{array}{l} \text{O.K} \\ \text{O.K} \end{array} \right.$ ; further instances are furnished by potassium aluminate, potassium plumbite, etc.

Finally, it should be borne in mind that, in acid liquors, a permanent precipitate can first be obtained by means of potassium hydroxide when all of the free acid has been saturated by this reagent. The behavior of sodium hydroxide is precisely similar to that of potassium hydroxide.

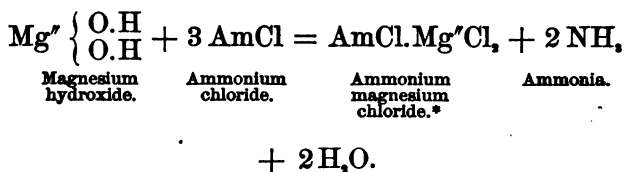
4) *Ammonia*,  $\text{NH}_3$ . Ammonia is a combination of one atom of trivalent nitrogen with three atoms of hydrogen:  $\text{N}''' \text{H}_3$ . At ordinary temperatures it is a colorless gas of extremely pungent odor, and is absorbed in large quantities and with remarkable energy by water. This aqueous solution is employed as a reagent. The action of aqueous ammonia upon the solutions of metals is varying, but, for the most part, is similar to that of potassium hydroxide; it then comport itself like a solution of ammonium hydroxide ( $\text{NH}_3 \cdot \text{O.H} = \text{Am.O.H} = \text{NH}_3 + \text{H}_2\text{O}$ ) and precipitates metallic hydroxides with attendant formation of ammonium compounds:



Many metallic hydroxides dissolve in excess of ammonia, forming compounds, the constitution of which have not been ascertained with certainty. If, for example, a small quantity of ammonia be added to a solution of copper sulphate there is precipitated at first a basic salt, which, however, dissolves with extraordinary readiness in an excess of ammonia; the compound thus formed consists of:  $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$  ammonio-cupric sulphate; other metallic oxides behave in the same way. From solutions of mercury oxides, ammoniacal mercury compounds are at once precipitated.

Ammonia displays a peculiar behavior in another respect; certain metallic oxides which are precipitated from neutral solutions by ammonia are not precipitated by the same reagent from acid solutions even when they are of themselves insoluble in ammonia. Magnesium oxide and those metallic oxides which are isomorphous with it furnish instances of this sort. The salts of these oxides form with ammonium salts peculiar double salts, which are not decomposed by free ammonia; the tendency to the formation of such salts is so great that the metallic hydroxides concerned in this matter dissolve very easily in the aqueous solutions of ammonium salts; thus, magnesium hydroxide dissolves very readily in a solution of ammonium

chloride, forming ammonium-magnesium chloride .  
and free ammonia :



The precipitation of magnesium oxide and of the other similar ones from neutral solutions by ammonia, therefore, may be completely prevented by the addition of a sufficient quantity of ammonium chloride ; if the solution be acid, the first portions of ammonia added naturally serve to produce a salt of ammonium which itself, as just explained, prevents the precipitation of such oxides. In such cases it is therefore necessary to neutralize the free acid by sodium carbonate or sodium hydroxide before adding the ammonia ; if ammonia be then added to this neutral solution, precipitation occurs. But even under these circumstances the precipitation is not complete, since

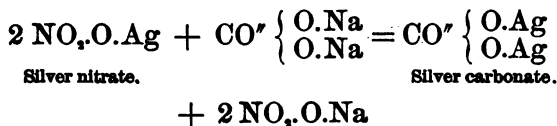
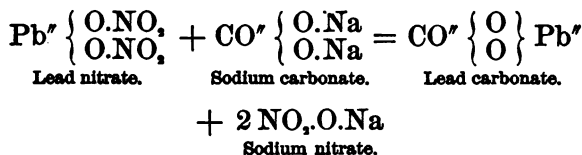
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\* Such "double salts" are regarded as peculiar cases of molecular addition. AmCl is itself a molecule in which all atomic valences are already saturated; the same is true of Mg'Cl<sub>2</sub>, and there are no atomic valences left for the connection of these two molecules, which are held together, nevertheless, by their *molecular* affinities. As the study of atomic valence progresses it may become possible to do away with this conception of molecular addition and to reduce all compounds to the case of true atomic constitution based exclusively upon the valences of the elementary atoms (see note on double cyanides, page 81). Indeed, at the present stage of our studies, it is evident that, whatever the connecting agency for the two molecules of a double salt is, its source is to be referred back to their individual atoms.

the salt of ammonium which forms in the reaction retains a portion of the oxide in solution.

5) *Sodium Carbonate*,  $\text{CO} \begin{Bmatrix} \text{O.Na} \\ \text{O.Na} \end{Bmatrix}$

Sodium carbonate is the neutral sodium salt of dibasic carbonic acid;\* that is, a combination of the bivalent radical carbonyl  $(\text{CO})''$  with two atoms of bivalent oxygen, each of which latter atoms is connected by its remaining valence to one atom of sodium:  $\text{CO}'' \begin{Bmatrix} \text{O.}''\text{Na} \\ \text{O.}''\text{Na} \end{Bmatrix}$ ; it is a colorless salt, easily soluble in water, yielding a solution which is of an alkaline reaction. When added to the solutions of other metals it effects always a double decomposition, the sodium atoms changing places with the atoms of the other metal:

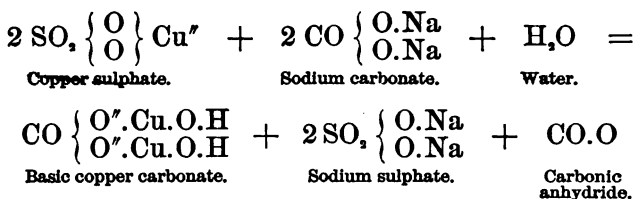


The carbonates thus formed, excepting those of alkalis and the thallium salt, are insoluble in water; instead of neutral salts, basic salts are often

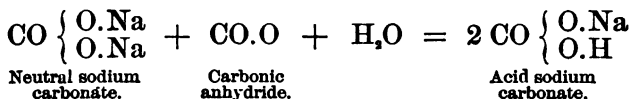
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\* See note, page 118.

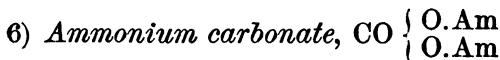
formed, in consequence of which carbonic anhydride is evolved even when the sodium carbonate is added to a perfectly neutral solution of a metallic salt :



If, however, an excess of sodium carbonate be added in the first place, the liberated carbonic anhydride does not escape as a gas, but at once forms with the excess of sodium carbonate an acid sodium carbonate :



All carbonates insoluble in water are dissolved by dilute acids, whereby carbonic anhydride is separated and immediately evolved in the gaseous state, and the salts are dissolved in the liquor, with effervescence. Hence, a precipitate from an acid metallic solution by sodium carbonate cannot be permanent until all of the free acid has been neutralized.



The composition of this salt corresponds fully to that of sodium carbonate; in place of the two atoms of sodium stand the two atom-groups,  $\text{NH}_4$ , ammonium :  $(\text{CO})'' \left\{ \begin{array}{c} \text{O.NH}_4 \\ \text{O.NH}_4 \end{array} \right\}$



The action of this reagent is quite similar to that of sodium carbonate, only that the ammonium carbonate is often capable of redissolving the precipitate when it is added in excess, giving rise to the formation of compounds similar to those discussed in the section devoted to ammonia.

The reagents which have hitherto been considered with respect to their behavior are chiefly adapted for the recognition of bases which may be present, excepting the potassium and sodium bases;\* sulphydric acid alone precipitates some metallic acids from acid solutions. The presence of acids cannot be demonstrated by these reagents for the reason that the basic radicals contained in the latter form soluble salts with all of the acids. All precipitates resulting from the employment of these reagents (excepting some by sulphydric acid) indicate the presence only of certain bases.\* For a recognition of the acids,\* therefore, other reagents must be employed which, conversely, shall precipitate the acids; to this requirement such bases respond as those which form a number of salts insoluble in water. From this it is patent that, fundamentally, each reaction may be employed in a twofold sense,

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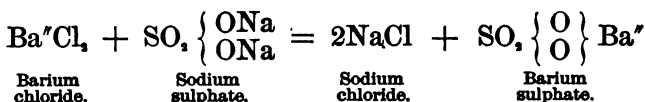
\* When we test for a metal, metallic oxide, etc., as in the preceding text, we may say in general that we test for the *base* in contradistinction to testing for the *acid*, though, strictly speaking, we test for the metallic radical which represents, or is part of, the base proper from which (according to note, page 38) the salt in solution may be regarded as derived. It should be remembered that true bases and true acids are compounds of hydrogen. The current phraseology of qualitative analysis about testing for the base and for the acid is not only convenient and serviceable, but in this sense justifiable.

namely, for the recognition of the base concerned in the reaction as well as for the acid ; but it is easy to understand that generally the reaction need be characteristic respecting only one of these two directions.

The principal reagents employed for the determination of acids are the three following : 1, barium chloride ; 2, lead acetate ; 3, silver nitrate. All three work in the same manner by double decomposition, through which their metals form insoluble salts with the acids which are to be determined. Here also the color, physical condition and solubility of the precipitates should be carefully observed.

1) *Barium chloride*, BaCl<sub>2</sub>.

Barium chloride is a combination of one atom of the bivalent metal barium with two atoms of chlorine. It is white, crystalline, and readily soluble in water. It gives precipitates with the salts of many acids by double metathesis :



The precipitates thus formed are to be tested respecting their solubility in dilute chlorhydric, or dilute nitric, acid. It is necessary to employ the diluted acids, because a solution of barium chloride gives, with concentrated chlorhydric or nitric acid, a crystalline precipitate of barium chloride or barium nitrate, which dissolves readily upon adding water. Moreover, if there be in the solution, which is to be

tested for an acid, oxides which are precipitated by chlorhydric acid (as silver oxide), barium nitrate must be employed in place of barium chloride, and the solubility of any resulting precipitate is tested with nitric acid.

2) *Lead acetate*,  $\text{Pb}'' \left\{ \begin{array}{l} \text{O.CO.CH}_3 \\ \text{O.CO.CH}_3 \end{array} \right.$

Neutral lead acetate is produced by the substitution of the basic hydrogen in two molecules of monobasic acetic acid:  $\text{CH}_3\text{CO.OH}$  by one atom of bivalent lead:  $\left\{ \begin{array}{l} \text{CH}_3\text{CO.O} \\ \text{CH}_3\text{CO.O} \end{array} \right\} \text{Pb}''$ ; it is colorless, readily crystallizable, and easy soluble in water. It works precisely like barium chloride. The resulting precipitates are to be tested as to their solubility in dilute nitric acid.

3) *Silver nitrate*,  $\text{NO}_3\text{O.Ag}$ .

Silver nitrate is formed by substitution of the basic hydrogen in one molecule of monobasic nitric acid,  $\text{NO}_3\text{O.H}$ , by one atom of univalent silver:  $\text{NO}_3\text{O.Ag}$ . It is colorless, crystallizes readily, and is easily soluble in water. Here also, in general, that which was stated under barium chloride holds good. Precipitates which this reagent gives are to be tested for their solubility in nitric acid and in ammonia; in the latter test care must be taken, of course, that no substances are present which would be precipitated from solution by ammonia.

The nine reagents which have been cited are so constantly employed that it is of importance to know with precision the deportment of each base and acid with respect to them; this is all the more necessary since with reference to them we divide the

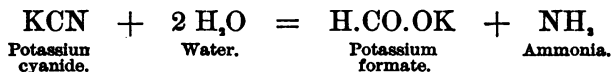
various bodies into groups which are precipitated by them from solutions. If, for instance, sulphydric acid effects a black precipitate in an acid solution, the presence of lead, copper, etc., is indicated; if this reagent produces no precipitate, then the absence of those metals is proved. The appearances which we observe upon the employment of the other reagents justify similar conclusions, which are rendered easily comprehensible by the foregoing remarks.

There are still other reagents which are not capable of such extended application as that which characterizes those just considered; rather are they employed only in certain cases to determine the presence or absence of a substance with the greatest possible definiteness and certainty, or to separate sharply one substance from another. In many cases an altogether peculiar chemical process occurs in the reaction which makes it characteristic for the substance under consideration, while in other cases, on the contrary, the distinguishing characteristic consists exclusively in the occurrence of a precipitate, often of a peculiar color, or in a change of color of the liquid without the separation of any precipitate, while in all other respects the course of the reaction expressed by formulas and equations is quite ordinary. As an example of the first sort of peculiar reactions may be mentioned the brown coloration which nitric acid causes in ferrous solutions; for the second sort, on the other hand, the precipitation of silver by chlorhydric acid and soluble metallic chlorides; the red coloration of ferric solutions by sodium acetate or potassium sulphocyanate, etc.

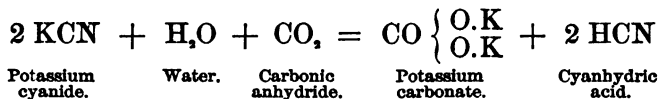
In the following, several reactions which are of frequent application will be treated in a general way; the remaining reactions, on the contrary, will be noticed specially in connection with each base or acid.

1) *Potassium cyanide*,  $\text{KCN} = \text{KCy}$ .

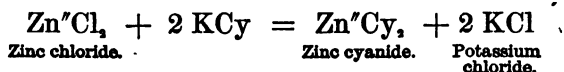
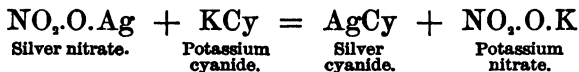
Potassium cyanide is a combination of one atom of potassium with one univalent atom-group, cyanogen, which is itself a combination of one atom of quadrivalent carbon with one atom of trivalent nitrogen:  $\text{K}(\text{C}^{\text{IV}}\text{N}^{\text{III}}) = \text{KCy}$ ; it is white, crystal line, very readily soluble in water; the aqueous solution soon decomposes with attendant evolution of ammonia (and a brown coloration):



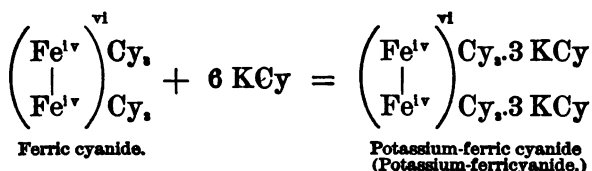
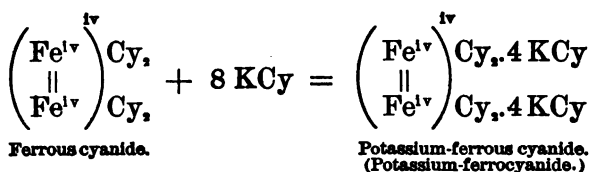
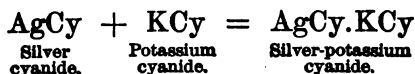
the odor of prussic acid [cyanhydric acid] is a consequence of the action of moist carbonic anhydride:



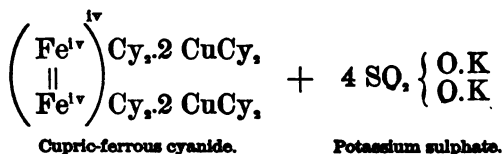
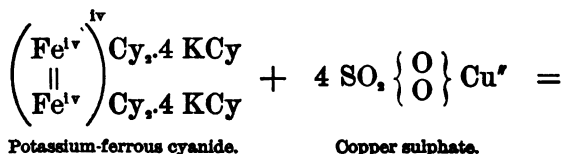
With the salts of most of the heavy metals it gives precipitates of metallic cyanides insoluble in water; these result from double metathesis:

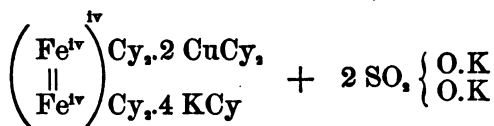
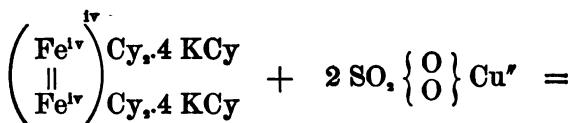


These metallic cyanides are easily soluble in an excess of potassium cyanide forming compounds with it, the so-called double cyanides :



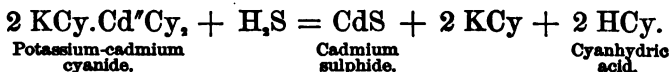
If solutions of these and similar double cyanides are brought into contact with metallic solutions, precipitates of insoluble double cyanides are formed :





Potassium-cupric-ferrous  
cyanide.

The chemical behavior of such double cyanides is very variable according to the metals contained in them. Some of them are easily decomposed by chlorhydric acid, sulphydric acid, etc.; others, on the contrary, are not. This variable deportment can be turned to account as a means of separating the respective metals from each other; while, for instance, potassium-cupric cyanide is not decomposed by sulphydric acid, this reagent precipitates cadmium completely, as cadmium sulphide, from solutions of potassium-cadmium cyanide:

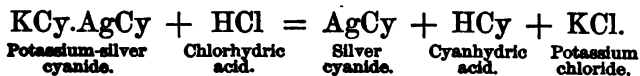


Potassium-cadmium  
cyanide.

Cadmium  
sulphide.

Cyanhydric  
acid.

Cobalt and nickel furnish a similar case. Corresponding distinctions are also manifested upon treatment to chlorhydric acid and sulphuric acid; potassium-silver cyanide is readily decomposed, separating silver cyanide:



Potassium-silver  
cyanide.

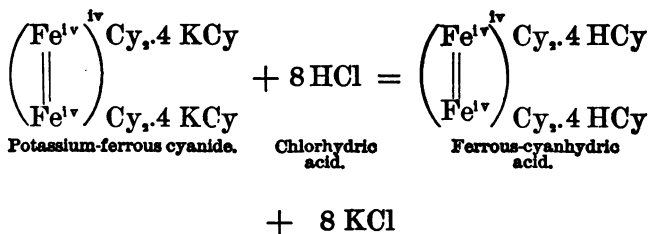
Chlorhydric  
acid.

Silver  
cyanide.

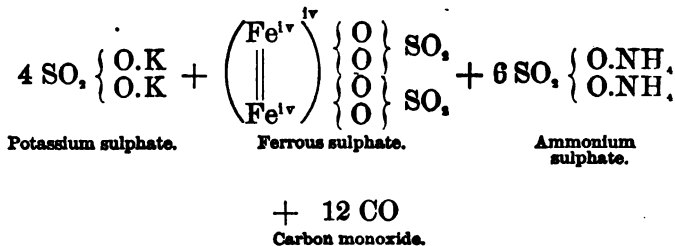
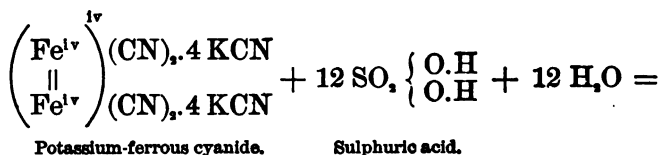
Cyanhydric  
acid.

Potassium  
chloride.

Potassium-ferrous cyanide, on the contrary, is so changed that the potassium contained in it is substituted by hydrogen :



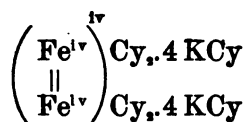
All simple and double cyanides, soluble and insoluble, are decomposed by heating them with a mixture of equal parts of sulphuric acid and water ; all of the cyanogen is converted into carbon monoxide and ammonia :



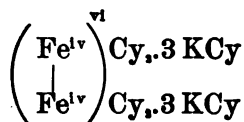


2) *Potassium-ferrous, and potassium-ferric, cyanide* (potassium-ferro, and potassium-ferri, cyanide).

These compounds belong to the double cyanides already mentioned, and to the more stable ones; potassium-ferrous cyanide crystallizes in large quadratic octohedrons,\* and consists of eight atoms of potassium, two atoms of quadrivalent iron, and twelve atom-groups of cyanogen:



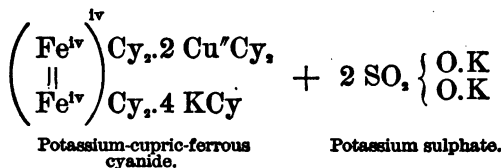
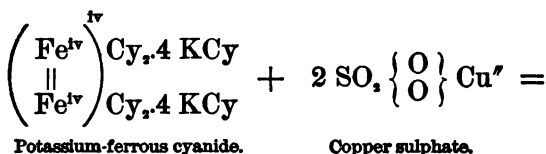
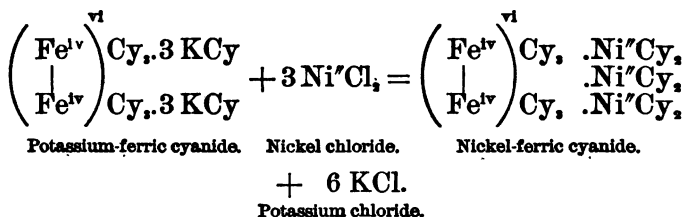
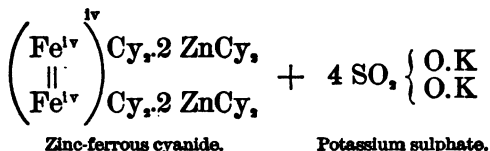
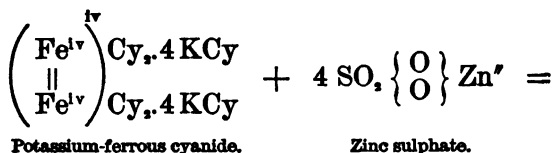
Potassium-ferric cyanide forms large red prisms, and is composed of six atoms of potassium, two atoms of quadrivalent iron, and twelve atoms of cyanogen:



The precipitates which these compounds produce in metallic solutions all result from double metathesis, by which the potassium is wholly or partially replaced by other atoms:

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\* Stauroscopic observations made by Fr. von Kobell, Mallard, and Wyruboff have revealed the fact that potassium-ferrous cyanide is not optically uniaxial but biaxial, and hence cannot belong to the tetragonal system. These authorities regard it as monoclinic. (Sitzungsberichte d. k. b. Acad. d. Wiss. zu München, 1878, 550-551; Ann. chim. phys. [4] xvi, 280; xxi, 271.)



From these equations it will be seen that all of the cyanogen and all of the iron contained in the original ferrous or ferric cyanide are contained in the precipitates and in the same mutual relations; on this account the hypothesis has been urged that

in these two compounds there exist special radicals, ferrocyanogen,  $(\text{Fe}''\text{Cy})'' = \text{Cfy}$ ; and ferridcyanogen,  $(\text{Fe}'''\text{Cy})''' = \text{Cfdy}$ . Both radicals have the same composition, but in the first case the iron is bivalent, in the second trivalent (the formulas then become half as great as those given above). All of the reactions of potassium-ferrous and ferric cyanides, however, may be just as easily explained if they be considered as double cyanides corresponding to the double chlorides, etc., as in the foregoing text.\*

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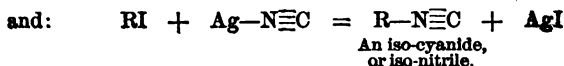
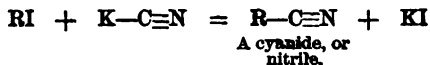
\* The whole subject of the ultimate constitution of many of the so-called double cyanides is largely a matter of conjecture. A few points, some of which have developed from recent studies of cyanogen compounds, and which present other views concerning the structure of some of the compounds cited in the text, may not be out of place.

We are here more especially concerned with the cyanogen radical, or rest, than with free cyanogen. This cyanogen radical may appear under a twofold guise, thus:  $-\text{C}\equiv\text{N}$  or  $-\text{N}\equiv\text{C}$ . In fact, two series of compounds are well known containing these two different forms of cyanogen rests, respectively. The compounds containing the first form, where the carbon atom of the cyanogen group is directly united to the rest of the compound, R, are called normal cyanides or nitriles; those of the second form, where the nitrogen of the cyanogen group is quinquivalent, and where it is joined directly to R, are called iso-cyanides or iso-nitriles. There is good reason to suppose that some of the metallic cyanides are of the normal, and some of the iso-, form. The potassium compound is regarded as of the normal form,  $\text{M}-\text{C}\equiv\text{N}$ , while the silver cyanide is thought to be of the iso-form,  $\text{M}-\text{N}\equiv\text{C}$ . Some of the reasons for these distinctions are the following: If a haloid compound (Cl, Br, I compound) of an alcohol radical (methyl,  $\text{CH}_3$ ; ethyl,  $\text{C}_2\text{H}_5$ , etc.) be treated to potassium cyanide, there are formed, by double metathesis, a potassium haloid compound, and a compound of the alcohol rest with a cyanogen rest of the  $-\text{C}\equiv\text{N}$  form. If, however, we employ silver cyanide instead of the potassium cyanide, we obtain a compound containing cyanogen of the iso-form,  $-\text{N}\equiv\text{C}$ . Hence, it seems likely that, in potassium cyanide, the cyanogen rest

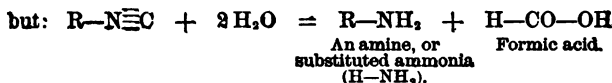
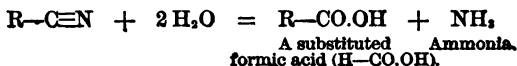
3) *Acids.*

In the section devoted to the action of the three general reagents for acids attention was called to the

is present in the form  $\text{—C}\equiv\text{N}$ ; and in silver cyanide, as  $\text{—N}\equiv\text{C}$ . The reactions just described may be essentially represented as follows:

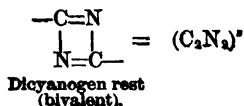


Argument for the structure of these metallic cyanides, founded upon such reactions, is not conclusive. That these compounds of the alcohol rests with cyanogen are really so constituted is shown by their decomposition products:

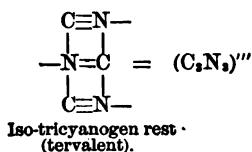
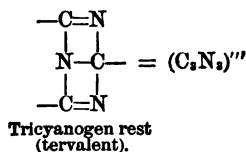
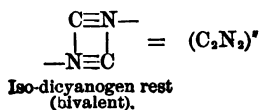


Finally, it is not unlikely that one and the same simple cyanide may isomerize now into the one form,  $\text{RCN}$ , now into the other,  $\text{RNC}$ , under varying conditions, among which, perhaps, temperature may be regarded as the most important.

A very important property of these cyanogen rests is their tendency to polymerize, that is, to unite and condense to form a radical of higher molecular weight, of the same percentage composition:  $(\text{C}_2\text{N}_2)^n$ . The structure of such polymeric forms is not known with certainty, but a plausible constitution, which accords well with established facts, has been assigned (see Wislicenus's edition of Strecker's *Lehrb. der org. Chem.* 6te Aufl. S. 94):



fact that all of the precipitates resulting from these tests were to be examined concerning their solubility in certain acids, since some of them are soluble



Further, we may suppose, with reason, that a polycyanogen group occurs containing both the normal and the iso-form:



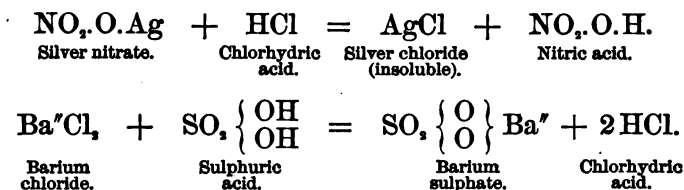
Whatever may be the ultimate constitution of such condensed cyanogen groups, it is especially important to bear in mind that for every single CN group so condensing, a free valence is brought into the resulting polymerized product; thus we have:



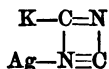
It now seems probable that, in all of the so-called double cyanides, the cyanogen is present in such polymerized forms. Such a conception at least obviates the necessity of a "molecular addition" in the sense of that expression respecting double salts, and brings these under the more ordinary category of atomic constitution, based exclusively upon the valences of the several atoms.

From what has been said of potassium cyanide, and of silver

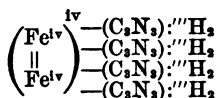
therein, while others are insoluble. The latter, insoluble precipitates, therefore, may also be obtained by the addition of the free acid to the metallic solution, but the former, soluble ones, cannot be so produced. The action of the acid in this case is based upon double metathesis; the free acid added to the solution forms with the metallic oxide present an insoluble compound, while the acid of the salt which was originally present is set free, and generally remains in solution:



cyanide, and of polymerization, the following formula for the double potassium-silver cyanide seems plausible:

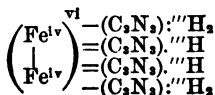


Ferrous-cyanhydric acid becomes:



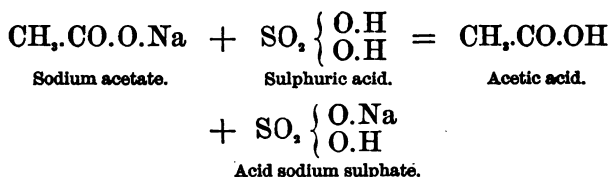
If we substitute, in this formula, atoms of metal for atoms of H, we obtain the respective metallic ferrous cyanide, just as metallic chlorides are derived from HCl by substitution of M' for H'.

The metallic ferric cyanides may be likewise regarded as derived from ferric cyanhydric acid of the constitution:



The entire process, then, consists of the exchange of places between the basic hydrogen of the added free acid and the metallic atom of the salt present.

Similar processes may also occur without the formation of a precipitate, as when the acid which is added is stronger than the acid contained in the salt in solution: a solution of sodium acetate is quite odorless, but if sulphuric acid be added the pungent odor of acetic acid is at once perceptible; a chemical reaction has taken place, of which the products are acid sodium sulphate and acetic acid:



If the liberated acid is more volatile than the one which was added, then it (in general, the more volatile one) may be completely expelled from the resulting mixture by proper application of heat; if the mixture of acetic acid and acid sodium sulphate be distilled, the acetic acid volatilizes completely, and may be collected in the proper apparatus. (If, on the contrary, the separated acid is less volatile than that acid which was added, the latter acid will be volatilized by subsequent heating, and the original compound regenerated; in this sense silicic acid expels sulphuric acid from potassium sulphate at the temperature of fusion, forming potassium silicate.)

If, therefore, it is desired to ascertain whether an easily volatile acid be present in a substance, sul-

phuric acid is poured upon it, and, if necessary, heat is applied ; an evolution of acid vapors demonstrates the presence of a volatile acid.

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## CHARACTERISTIC AND SPECIAL REACTIONS OF THE MOST IMPORTANT BASES AND ACIDS.

In this section a succinct presentation of characteristic reactions will be given, and particularly of such reactions as involve special chemical processes ; an equation for the course of the reaction will be given only in cases where it is not rendered plain by the foregoing considerations.

### I. BASES.\*

#### A) METALLIC OXIDES, FROM THE ACID SOLUTIONS OF WHICH PRECIPITATES ARE PRODUCED BY SULPHYDRIC ACID.

a) *The precipitated metallic sulphides are insoluble in ammonium sulphide.*

##### 1) *Cupric oxide.*

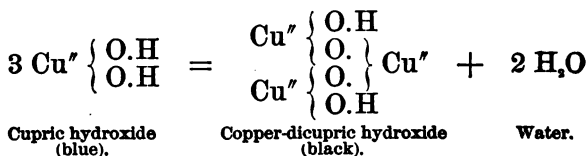
The solutions of this oxide are especially distinguished by their behavior toward a solution of sodium hydroxide, solution of ammonia and ammonium carbonate, and solution of potassium-ferrous cyanide. The light-blue precipitate produced by

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\* See note, page 69



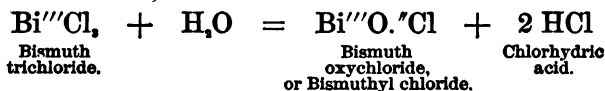
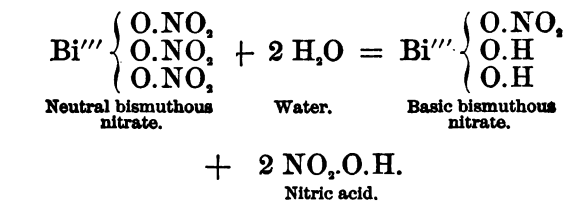
sodium hydroxide solution is cupric hydroxide,  $\text{Cu}''(\text{OH})_2$ , which upon heating, or long standing, liberates water, and becomes black in consequence :



With ammonia and ammonium carbonate there are formed at first light-blue or bluish-green precipitates, which dissolve in excess of the precipitant very easily, producing a beautiful azure-blue color, and forming ammonio-copper compounds (see page 65). Potassium-ferrous cyanide gives, in acid solutions, precipitates of copper-ferrous cyanide (see page 74) of a red to brownish-red color.

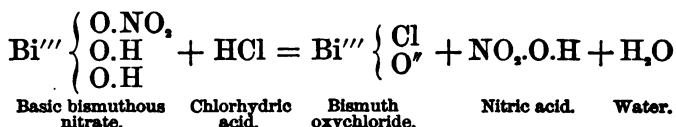
2) *Bismuthous oxide.*

Its solutions are distinguished by their behavior toward water, by which they are precipitated :



Here the water acts as a base, inasmuch as it abstracts a portion of the nitric acid radicals from the bismuth salt ; but it acts also as an acid, since its

elements enter into the basic salt in the place of the acid groups  $\text{NO}_2\text{O}$  which have been expelled. In the case of bismuth chloride, the corresponding compound,  $\text{Bi}'''(\text{OH})_2\text{Cl}$ , appears to be incapable of existence, decomposing at once into  $\text{Bi}''' \text{O} \cdot \text{Cl} + \text{H}_2\text{O}$ . Bismuth oxychloride is almost absolutely insoluble in water, while the basic nitrate is only difficultly soluble; hence the latter is not precipitated from somewhat acid solutions which are already dilute upon the further addition of water, while even in such dilute solutions a precipitation immediately ensues upon the addition of some chlorhydric acid or of a soluble metallic chloride:



All basic bismuth compounds are readily soluble in concentrated acids; but tartaric acid does not cause the cloudiness occasioned by water in bismuth solutions to disappear.

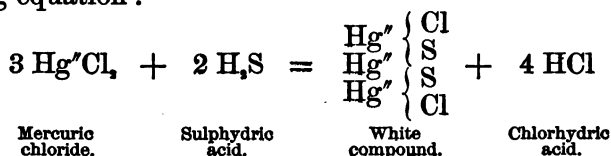
### 3) *Cadmium oxide.*

For the solutions of this metallic oxide the yellow precipitate, insoluble in ammonium sulphide, produced by sulphydric acid is characteristic. The hydroxide is soluble in ammonia, but not in solution of sodium hydroxide (distinction from bismuth, lead and zinc); cadmium carbonate is likewise insoluble in ammonium carbonate.

### 4) *Mercuric oxide.*

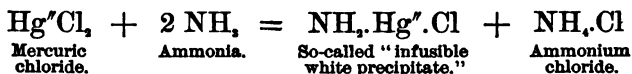
Its solutions are distinguished from all others by their behavior toward sulphydric acid. If this re-

agent be added in small quantities to an excess of the solution of the salt there is first formed a white precipitate insoluble in water and dilute acids, which becomes yellow upon further addition of sulphydric acid, then brown, and finally black, being converted into mercuric sulphide. The white precipitate which forms at first is a combination of mercuric sulphide with mercuric chloride, mercuric nitrate, etc. ; its formation takes place in accordance with the following equation :



The black mercuric sulphide is insoluble even when boiled in dilute nitric acid (distinction from lead, copper, bismuth, silver, cadmium). In alkaline sulphides it is insoluble ; but if some solution of sodium hydroxide be added, it dissolves.

Solution of sodium hydroxide in excess precipitates yellow anhydrous mercuric oxide (see above).\* Ammonia produces white precipitates, some of which are soluble in excess of the precipitant (when mercuric nitrate is employed), others insoluble which contain the elements of ammonia (see above).† Thus, in a solution of mercuric chloride, ammonia effects a white, insoluble precipitate :



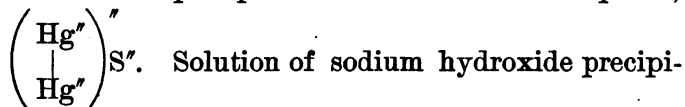
\* Under the reagent potassium (or sodium) hydroxide, page 68.

† Under the reagent ammonia, page 65.

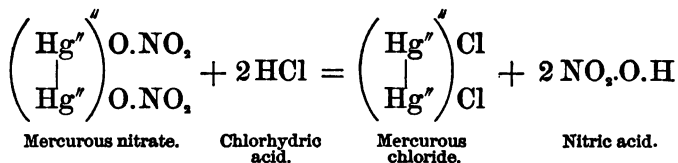
Similar precipitates are produced by the caustic alkalies and the alkaline carbonates when the solution of mercuric oxide contains ammonium salts. It should be remarked that, in some respects, the chemical behavior of a solution of mercuric chloride is different from that of a solution of mercuric nitrate: while the latter is precipitated by sodium phosphate, oxalic acid, potassium-ferric cyanide, and urea, the former remains clear when these reagents are applied.

5) *Mercurous oxide.*

From solutions of this metallic oxide, sulphydric acid at once precipitates black mercurous sulphide,



tates black mercurous oxide. Ammonia and ammonium carbonate also precipitate black compounds which contain the elements of ammonia. Chlorhydric acid and soluble chlorides precipitate white mercurous chloride (calomel) in accordance with the equation:



this precipitate is insoluble in water and dilute acids, soluble in hot concentrated nitric acid or aqua regia; it becomes blackened by ammonia, but is not dissolved (distinction from lead and silver).

6) *Argentio oxide.*

Solutions of this oxide are quite sharply characterized by their reactions with chlorhydric acid and soluble metallic chlorides, by which, even in the most dilute solutions, a white precipitate of silver chloride, insoluble in water and dilute acids, is formed (see page 43). If the silver chloride be precipitated in the dark it is perfectly white while fresh, but becomes colored violet to black in the light, chlorine being set free; it is easily soluble in ammonia, and may readily be completely precipitated again from such solution by dilute nitric acid. In the alkaline chlorides, as well as in hot, concentrated chlorhydric acid, it is somewhat soluble; hence, when endeavoring to ascertain whether or not ammonia has extracted small quantities of silver chloride from a precipitate effected by chlorhydric acid, the ammoniacal liquor should not be acidified with chlorhydric acid, since, under such circumstances, small quantities of the silver chloride would remain dissolved. Silver chloride is soluble also in potassium cyanide, forming thereby potassium-silver cyanide; it dissolves also in sodium thiosulphite.

Solution of sodium hydroxide precipitates brown silver oxide.

7) *Plumbous oxide.*

The salts of this metallic oxide are also precipitated by chlorhydric acid and soluble metallic chlorides; the white precipitate of lead chloride however, is not absolutely insoluble in water, but only difficultly soluble, and disappears, therefore, upon the addition of much water; indeed, it is not produced at all in dilute solutions. In hot water

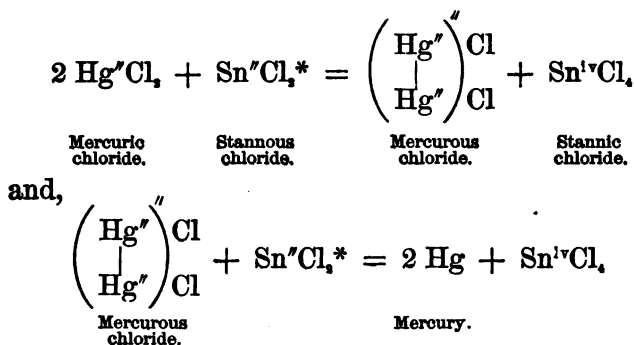
and in hot concentrated chlorhydric acid it is tolerably soluble and crystallizes in needles upon cooling; in dilute chlorhydric acid or nitric acid it is less soluble than in pure water; ammonia does not dissolve it, and the precipitate remains white. Solutions of this oxide are also precipitated by dilute sulphuric acid (see page 71); the lead sulphate is not absolutely insoluble in nitric acid, but is precipitated from this solution by excess of sulphuric acid; it is soluble in sodium hydroxide, basic ammonium tartrate, and in concentrated chlorhydric acid. It should be mentioned that solutions of lead oxide containing much chlorhydric acid are sometimes precipitated red by sulphydric acid; there is then formed a compound similar to the white precipitate mentioned under mercuric oxide. Sodium hydroxide solution and ammonia precipitate white lead hydroxide,  $\text{Pb}'' \begin{Bmatrix} \text{O.H} \\ \text{O.H} \end{Bmatrix}$  which is insoluble in an excess of the former precipitant.

b) *The precipitated metallic sulphides are soluble in ammonium sulphide.*

8) *Stannous oxide.*

The solutions of this oxide are precipitated brown by sulphydric acid; the precipitate of stannous sulphide,  $\text{Sn}''\text{S}$ , is insoluble in colorless ammonium sulphide, but soluble in the yellow; the reaction here involved has been already explained. All of the solutions of stannous oxide, and especially the chlorhydric acid solution or solution of stannous chloride, evince a strong tendency to form higher grades of oxidation, hence they act as energetic re-

ducing agents ; ferric chloride becomes reduced to ferrous chloride, and, notably, mercuric chloride is first reduced to mercurous chloride, and subsequently to metallic mercury :



This reaction is very delicate and characteristic. Sodium hydroxide and ammonia precipitate stannous hydroxide, which is soluble in excess of the former reagent ; if this solution does not contain too much of the caustic soda it deposits stannous oxide upon boiling. Alkaline carbonates likewise precipitate only stannous hydroxide, with simultaneous evolution of carbonic anhydride (see page 67).

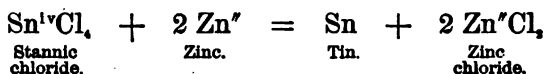
9) *Stannic oxide.*

From the solutions of this oxide caustic alkalies and their carbonates precipitate stannic hydroxide, which is soluble in solution of sodium hydroxide. The yellow to light-brown stannic sulphide is readily soluble in ammonium sulphide (see page 61), but is insoluble in ammonium carbonate and acid potassium sulphite (distinction from arsenic). Metallic

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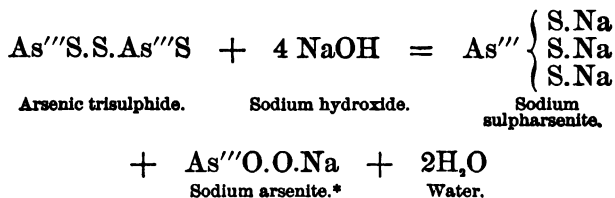
\* See note, page 12.

zinc, in presence of free chlorhydric acid, precipitates metallic tin, which, if it be again dissolved in chlorhydric acid, gives the reactions for stannous chloride :



10) *Arsenious oxide* [arsenious anhydride].

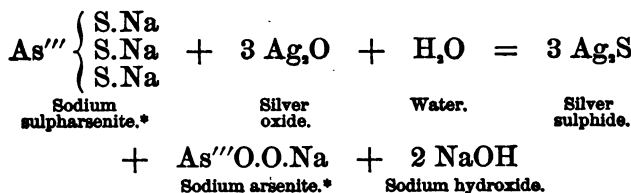
The pure aqueous solution of arsenious oxide is not precipitated by sulphydric acid, but is only colored yellow ; the precipitation commences immediately, however, upon the addition of a few drops of chlorhydric acid ; the yellow precipitate is characteristic in its behavior : it is readily soluble in ammonia, in caustic alkalies and their carbonates, as well as in acid potassium sulphite. The solubility of the arsenic trisulphide in the caustic alkalies or their carbonates depends upon the simultaneous formation of a sulpho, and an oxygen, salt :



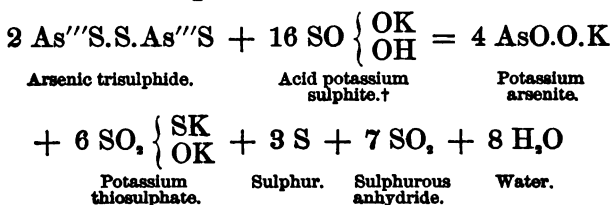
If an alkaline carbonate be employed, carbonic anhydride is either evolved or is retained by an excess of the alkaline salt ; if chlorhydric acid be added to the alkaline solution all of the arsenic is re-precipitated as trisulphide (see page 62); but if an ammoniacal solution of silver nitrate is added silver sul-



phide is formed, and only oxygen salts remain in the liquor. The action of the silver oxide is thus shown :



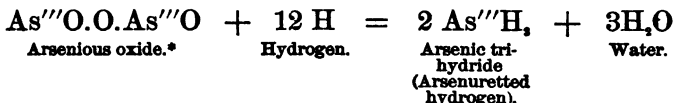
The solution of the trisulphide in acid potassium sulphite takes place with attendant formation of potassium thiosulphate :



\* It has been generally held that arsenious acid functionates as a tribasic, and as a monobasic, acid:  $\text{As} \left\{ \begin{array}{l} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \right.$  or  $\text{AsO.OH}$ . In accordance with this tribasic form the corresponding sulph-acid would be, as in the text,  $\text{As} \left\{ \begin{array}{l} \text{SH} \\ \text{SH} \\ \text{SH} \end{array} \right.$ . J. Thomsen (Deut. Chem. Ges. Ber. vii. 935) argues that arsenious acid is dibasic, and perhaps monobasic.

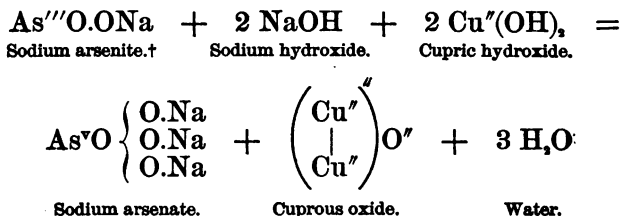
† Sulphurous acid (hypothetical) is now regarded by some writers as  $\text{SO}_2 \left\{ \begin{array}{l} \text{H} \\ \text{OH} \end{array} \right.$  which is a monobasic acid inasmuch as it has but one hydroxyl group, but which admits of ready substitution of its remaining atom of H by M'. Accordingly, the salt hitherto regarded as acid potassium sulphite becomes a neutral salt, while the salt usually called neutral potassium sulphite becomes potassium potassium-sulphite, *i.e.* a salt of potassium-sulphurous acid.

By treatment to hydrogen *in statu nascendi* (zinc with HCl) all of the oxygen of the arsenic trioxide may be abstracted, the hydrogen taking its place:



The formation of the arsenic trihydride in this way is perfectly analogous to the formation of ammonia from nitrous acid (see page 22). It should be stated that arsenuretted hydrogen is exceedingly poisonous; if it be conducted through a tube heated to redness it is decomposed into hydrogen and arsenic vapor.

Arsenious oxide may be distinguished from arsenic oxide by its behavior toward an alkaline solution of copper; if arsenious oxide be dissolved in a solution of sodium hydroxide, and a copper solution be added, a solution of a beautiful blue color results, which, upon boiling, separates red cuprous oxide:



11) *Arsenic oxide* [arsenic anhydride].

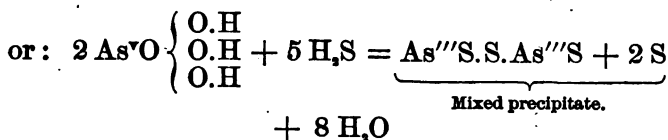
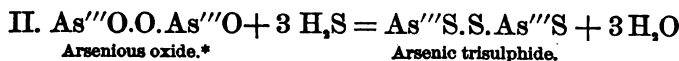
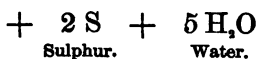
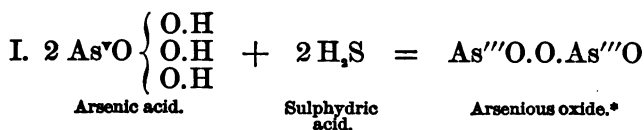
Acid solutions of this oxide are especially characterized by their behavior toward sulphydric acid;

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\* See note, page 27. † See note, page 93.

if this gas be conducted into a solution of arsenic oxide, there is, at first and especially in the cold, no perceptible reaction; after long standing (sometimes from twelve to twenty-four hours), more quickly by heating, a precipitate forms, consisting at first of sulphur, afterwards of arsenic trisulphide, since the arsenic oxide is first reduced by the sulphydric acid to arsenious oxide, which is then precipitated as trisulphide by the added fresh portions of the sulphydric acid.

Accordingly, the precipitation of arsenic acid by this reagent is completed in two phases, and the precipitate, which contains five atoms of sulphur to two of arsenic, is not a proper chemical compound, but a mixture of arsenic trisulphide and of free sulphur in that proportion. The reactions occur as follows:




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\* See note, page 27.

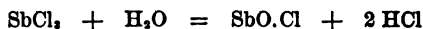
Arsenic acid comports itself with respect to bases like phosphoric acid, and forms, as phosphoric acid does, an ammonium-magnesium double salt (see below, under phosphoric acid).

12) *Antimonous oxide* [antimonous anhydride].

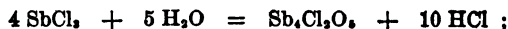
Solutions of this oxide are distinguished by the orange-red precipitate which sulphydric acid effects; the precipitate is readily soluble in ammonium sulphide, but insoluble in ammonium carbonate and in acid potassium sulphite (distinction from arsenic). By caustic alkalies and their carbonates only the antimonyl hydroxide [ $\text{SbO.OH}$ , antimonous acid] is precipitated. Water precipitates the so-called powder of Algaroth (of variable composition), or basic antimony chloride; this reaction is the same as the corresponding one for bismuth, only the antimony precipitate is readily soluble in tartaric acid.\* If the oxide be treated to nascent hydrogen, antimonuretted hydrogen [antimony trihydride] is formed, in strict analogy to the formation of arsenuretted hydrogen.

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\* According to the amount of water added to a solution of antimony trichloride the precipitate may be as follows:



or, by large quantities of water :



by a great excess of water, and after longer action of the water, there is formed antimonous oxide:



(See Sabanejew, *Zeits. für Chem.* [2] vii. 204; also Menschutkin, *Analyt. Chem. Deutsch. Ausg.* 1877, S. 281.)

- B) METALLIC OXIDES, THE ACID SOLUTIONS OF WHICH ARE NOT, BUT WHOSE ALKALINE SOLUTIONS ARE, PRECIPITATED BY SULPHYDRIC ACID.

13) *Zinc oxide.*

Ammonium sulphide precipitates white zinc monosulphide from solutions of this metallic oxide, which dissolves easily in dilute chlorhydric acid, even when the acid is cold; it is noteworthy that sulphydric acid precipitates a part of the zinc from perfectly neutral solutions until the free acid hereby produced prevents further precipitation, while, on the contrary, such acid solutions as contain only a free organic acid (as acetic acid, lactic acid, etc.) are completely precipitated by this reagent.

Ammonia precipitates zinc hydroxide, which dissolves readily in an excess of the precipitant as well as in ammonium chloride (distinction from aluminium oxide).

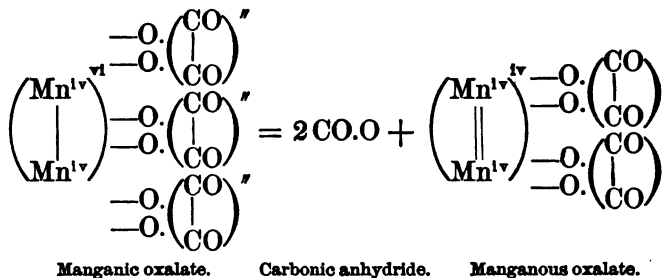
14) *Manganous oxide.\**

Ammonium sulphide precipitates a flesh-colored precipitate of manganous sulphide, which dissolves easily even in acetic acid. Sodium hydroxide solution and ammonia (if there is no ammonium chloride present) precipitate white manganous hydroxide, which, in contact with the air, is rapidly further oxidized, becoming darker colored and finally blackish-brown. The manganic hydroxide formed is readily soluble in a cold, concentrated solution of

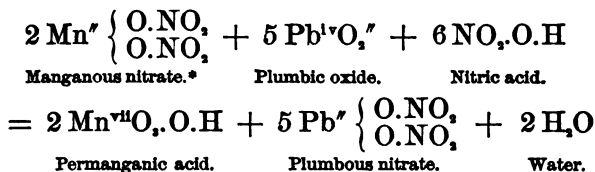
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\* Molecular formulas for manganous and manganic compounds should be written analogously to those for ferrous and ferric compounds, if it be desirable to be strictly consequential in this matter. (See pp. 18, 26, 45.)

oxalic acid,  $\left[ \begin{array}{c} \text{CO.OH} \\ | \\ \text{CO.OH} \end{array} \right]$ , producing a violet-red solution which soon decolorizes with attendant liberation of carbonic anhydride :



If a solution of manganous nitrate, free from chlorine, be boiled with plumbic oxide  $[\text{PbO}_2]$  and nitric acid, the liquid assumes a deep violet-red color, due to the formation of permanganic acid :

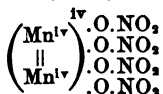


15) *Cobaltous oxide.*

In solutions of this oxide ammonium sulphide effects a black precipitate of cobaltous sulphide, which is almost insoluble in dilute, cold chlorhydric

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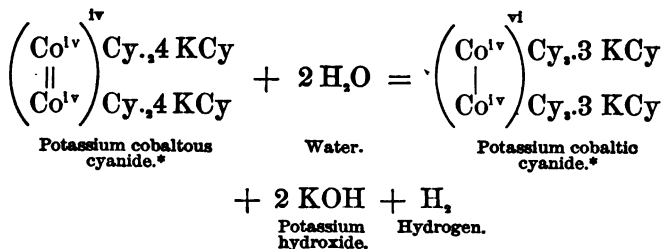
\* Perhaps it would be as well, here, to write



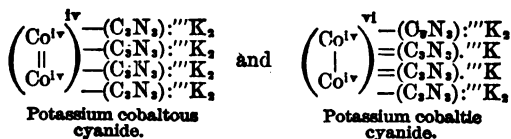
in accord with the "ous" manganese salt last mentioned, manganous oxalate.

acid (distinction from iron); from a solution acidified with acetic acid it is not precipitated by sulphuric acid. Ammonia occasions a blue precipitate, which dissolves easily in an excess of that precipitant; the resulting solution is distinguished for the avidity with which it absorbs oxygen from the air, becoming brown, whereupon it is found to contain ammoniacal cobaltic oxide compounds. Potassium

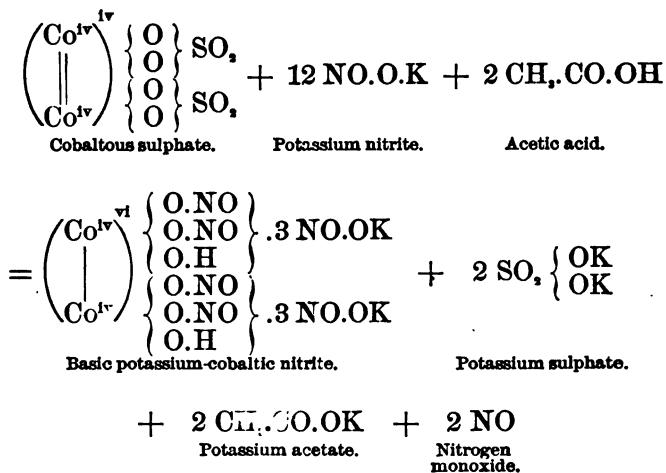
cyanide effects a brownish precipitate,  $\left(\begin{smallmatrix} \text{Co}^{\text{iv}} \\ || \\ \text{Co}^{\text{iv}} \end{smallmatrix}\right) \text{Cy}_2$  in cobaltous solutions, which dissolves in an excess of the potassium cyanide, forming at first the salt,  $8 \text{ KCy} \cdot 2 \text{ CoCy}$ .\*. If the solution of this compound be boiled, under the addition of some solution of potassium cyanide, hydrogen gas is liberated and potassium-cobaltic cyanide is formed, corresponding to potassium-ferric cyanide:



\* These complex cyanides may, and now probably should be, written as compounds containing cyanogen in polymeric forms according to note on page 79.



In cobaltous solutions acidified with acetic acid a concentrated solution of potassium nitrite, aided by gently warming the liquid, produces a yellow, pulverulent precipitate of potassium-cobaltic nitrite:



The equation indicates that the quadrivalent diatomic cobalt radical is converted into the sexivalent radical (since its two atoms are now held together by only one valence of each), and the two valences thus rendered available are each saturated by the radicals, hydroxyl, these latter being derived from the nitrous acid (which was liberated by the acetic acid), of which the other ingredients are evolved as nitrogen monoxide. Potassium-cobaltic nitrite is not insoluble in water and dilute acids, but is insoluble in a liquid which contains potassium nitrite.

16) *Nickelous oxide.*

Its solutions exhibit great similarity to those of



cobaltous oxide in their behavior, especially respecting ammonium sulphide, inasmuch as the precipitated nickelous sulphide is just as insoluble in dilute and cold acids as the cobaltous sulphide is; it is distinguished from the latter, however, in that it is slightly soluble in ammonium sulphide, especially when free ammonia is present, producing a brown-colored liquid.

By potassium cyanide or cyanhydric acid all of the nickel is precipitated as nickelous cyanide, which is soluble in potassium cyanide; this solution remains unchanged by boiling, and hence, after boiling, may be precipitated by chlorhydric acid (distinction from cobalt). Nickel solutions are not precipitated by potassium nitrite (distinction from cobalt). A further characteristic for nickel solutions is the blue color produced by the solution of the precipitates effected by ammonia, in an excess of that precipitant; this solution in ammonia absorbs no oxygen from the air.

17) *Ferrous oxide.*

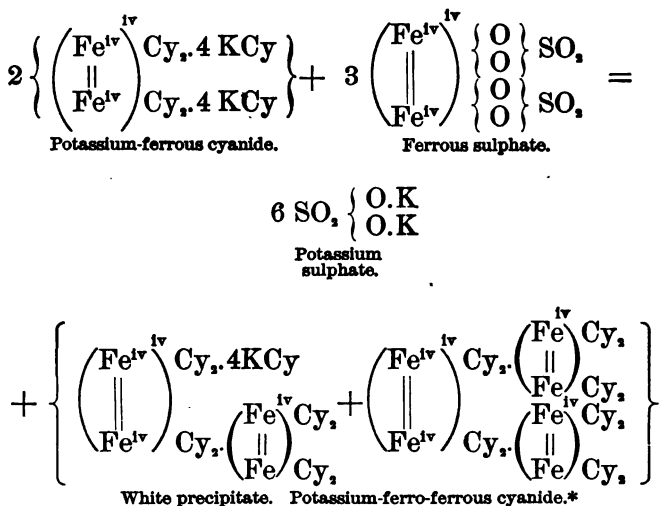
Solutions of ferrous oxide are precipitated black by ammonium-sulphide (when very dilute they are often only colored greenish); the precipitate dissolves easily in cold, dilute acids (distinction from cobalt and nickel). Caustic alkalis and their carbonates produce, at first, white precipitates of ferrous hydroxide and ferrous carbonate, which, however, absorb oxygen from the air, become rapidly green, then dingy brown to black, and finally reddish-brown. Ammonium chloride prevents the precipitation by ammonia (see page 65).

Potassium-ferrous cyanide produces in ferrous

solutions a bluish-white precipitate, which, in contact with the air or when treated to chlorine or to nitric acid, assumes a very beautiful blue color.

The precipitate is not pure ferrous cyanide  $\left( \begin{smallmatrix} \text{Fe}^{\text{iv}} \\ \parallel \\ \text{Fe}^{\text{iv}} \end{smallmatrix} \right) \text{Cy}_2$ ,

but, according to the varying conditions attending its formation, contains various quantities of potassium; most generally it is produced in accordance with the following equation :

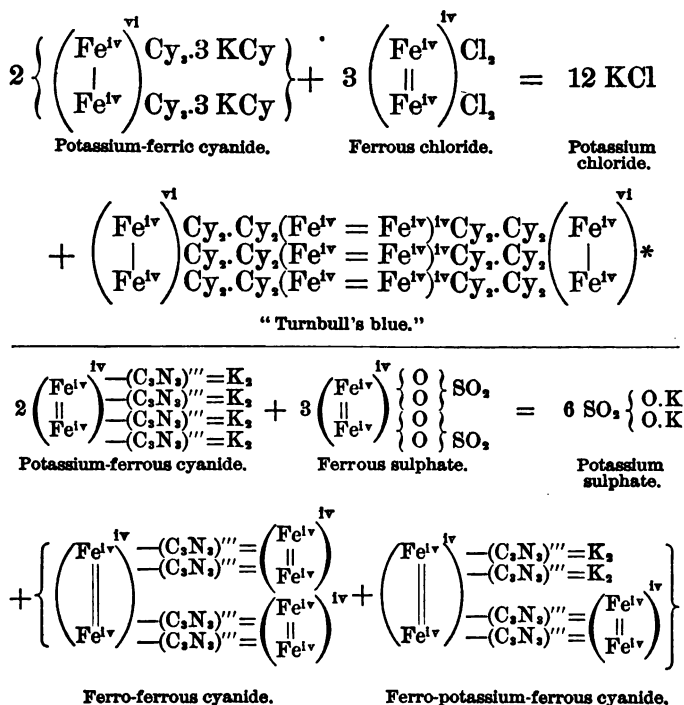



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\* This is to be regarded as a compound precipitate of a ferro-ferrous cyanide (*ferro* signifying that ferrous radicals substitute the potassium atoms of the potassium-ferrous cyanide, or the hydrogen atoms of the corresponding hydrogen-ferrous cyanide = ferrous-cyanhydric acid) and of a ferro-potassium-ferrous cyanide (see note, page 79). This reaction, in the sense of these notes on cyanides, may then be written:

The equation shows that the compound is produced by partial substitution of the potassium atoms of the potassium-ferrous cyanide by quadrivalent, diatomic radicals of iron [*i.e.*, by “ous” iron].

Potassium-ferric cyanide immediately produces in ferrous solutions, a blue precipitate, the so-called Berlin (Turnbull's) blue, which also often contains potassium; precipitated from strongly acid solutions, it is formed as follows:

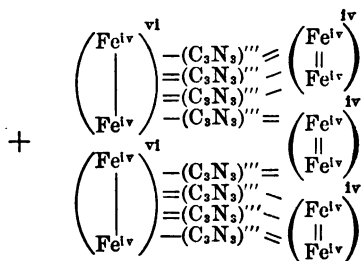
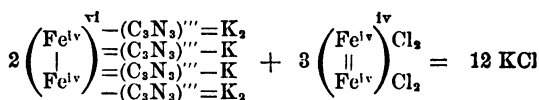
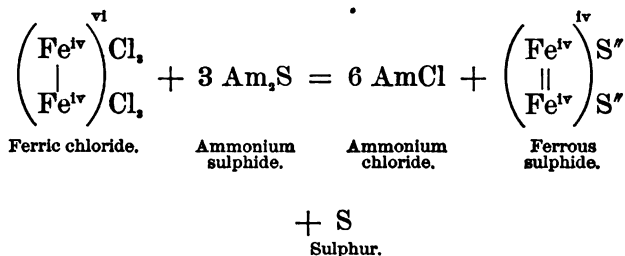


\* In harmony with the views set forth in these notes the reaction and compounds would be thus written:

Ferrous solutions are further distinguished for their tendency to absorb nitrogen monoxide gas, forming soluble, blackish-brown compounds (see under nitric acid).

18) *Ferric oxide.*

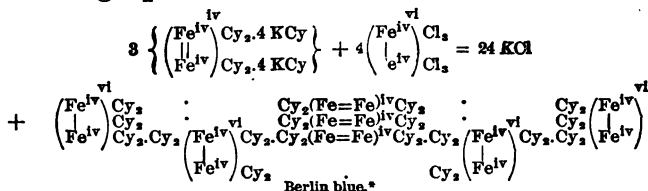
Solutions of this oxide are reduced by sulphydric acid, with separation of sulphur (see above, page 56). Ammonium sulphide produces a black precipitate consisting of a mixture of sulphur and ferrous sulphide :



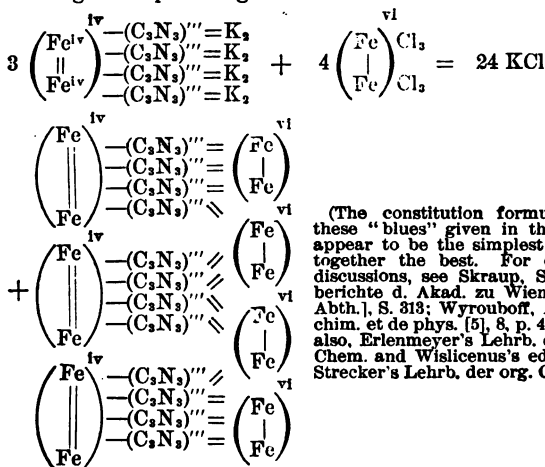
Turnbull's blue, or ferro-ferric cyanide (*ferro* indicating that *ferrous* molecules substitute the K atoms of the original potassium-ferric cyanide).

Caustic alkalis and their carbonates effect reddish-brown precipitates of ferric hydroxide. Potassium sulphocyanate imparts a dark blood-red color to acid solutions of ferric oxide, forming soluble ferric sulphocyanate by double decomposition (distinction from ferrous oxide).

Potassium-ferrous cyanide produces, at once, a precipitate of Berlin blue which, like the corresponding precipitate mentioned above, often contains some potassium. It forms according to the following equation :



\* According to the preceding notes this would be written:

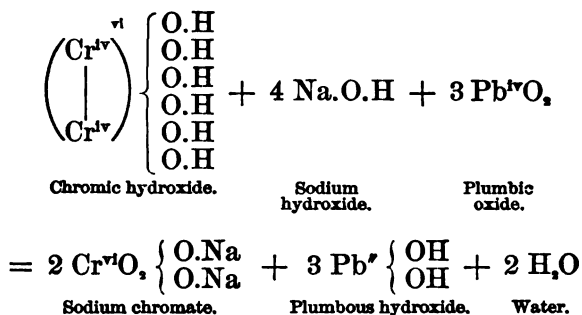


**Ferri-ferrous cyanide** (*ferri* indicating that *ferric* molecules have taken the place of the K atoms in the original potassium-ferrous cyanide).

C) METALLIC OXIDES, WHICH ARE PRECIPITATED AS HYDROXIDES BY AMMONIUM SULPHIDE FROM NEUTRAL SOLUTIONS.

19) *Chromic oxide.*

From solutions of this metallic oxide ammonium sulphide precipitates the hydroxide and not the sulphide (see p. 80). Caustic alkalies, as well as their carbonates, also precipitate chromic hydroxide, which dissolves readily in solution of sodium hydroxide, but is precipitated from such solution by boiling. If the alkaline (green) solution of chromic oxide be warmed with some plumbic oxide  $[PbO_2]$  it assumes a yellow color in consequence of the formation of sodium chromate:



The plumbous hydroxide formed remains dissolved in the excess of alkali.\*

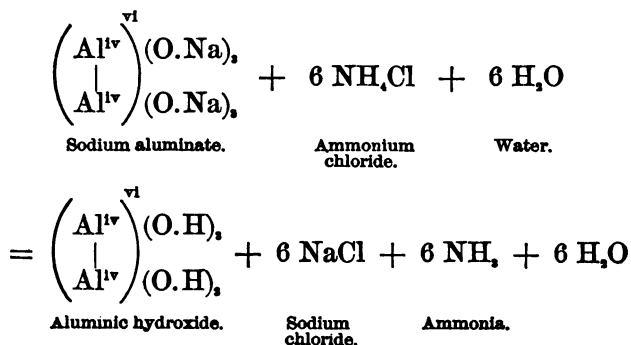
20) *Aluminic oxide*

Solutions of this oxide exhibit great similarity to those of chromic oxide in their behavior; this oxide

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\* The plumbous hydroxide acts toward the sodium hydroxide as an acid, forming sodium plumbite.

is also soluble in solution of sodium hydroxide, but is not precipitated from the solution by boiling. If, however, ammonium chloride be added, the aluminic oxide separates as a white, gelatinous precipitate [the hydroxide]; this is because the sodium hydroxide decomposes the ammonium chloride, forming sodium chloride and free ammonia; since the latter is almost wholly incapable of holding the aluminic oxide in solution it separates out. Small quantities of aluminic oxide dissolved in much soda lye are detected in this way with difficulty, and often quite elude observation, since, on the one hand, there is no means of determining when all of the free sodium hydroxide has been converted into sodium chloride by the ammonium chloride, and, on the other hand, large quantities of free ammonia dissolve a significant amount of aluminic oxide. A safer way, therefore, is to add just enough chlorhydric acid to the solution, which is alkaline with sodium hydroxide, to cause it to react acid, and then by the addition of a few drops of ammonia restore the alkaline reaction:

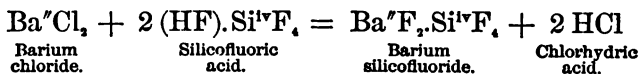


D) METALLIC OXIDES, THE SOLUTIONS OF WHICH ARE NOT PRECIPITATED BY AMMONIUM SULPHIDE, BUT ARE PRECIPITATED BY AMMONIUM CARBONATE.

21) *Barium monoxide.*

Solutions of this oxide are not precipitated by sulphydric acid, ammonium sulphide or ammonia; they are precipitated by solution of sodium hydroxide only when they are rather concentrated—the precipitate of hydrated barium hydroxide,  $(\text{Ba}'' \left\{ \begin{smallmatrix} \text{O.H} \\ \text{O.H} \end{smallmatrix} \right\} + 8 \text{H}_2\text{O})$ , is completely soluble in much water—and by alkaline carbonates even when more dilute. Barium carbonate is somewhat soluble in water containing carbonic anhydride in solution, but separates upon warming the liquid, especially upon the addition of some ammonia. Sulphuric acid precipitates barium sulphate even from the most dilute solutions (see above, page 44); solutions of sulphates effect the same result, notably even a solution of calcium sulphate, which immediately produces a precipitate in solutions of barium.

Silicofluoric acid produces a precipitate of barium silicofluoride (distinction from strontium and calcium):



Potassium dichromate precipitates yellow barium chromate, which is difficultly soluble in dilute acids (distinction from strontium and calcium).

22) *Strontium monoxide.*

Respecting sulphydric acid, ammonium sulphide, caustic alkalies and their carbonates, the solutions



of strontium monoxide manifest the same behavior which has been cited for barium monoxide. Sulphuric acid precipitates also solutions of strontium monoxide, but the precipitated strontium sulphate is not quite as insoluble in water and dilute acids as the barium sulphate, hence it happens that the solution of calcium sulphate does not effect a precipitate at once, but only after a few minutes. Potassium dichromate and silicofluoric acid do not precipitate strontium monoxide solutions (distinction from barium).

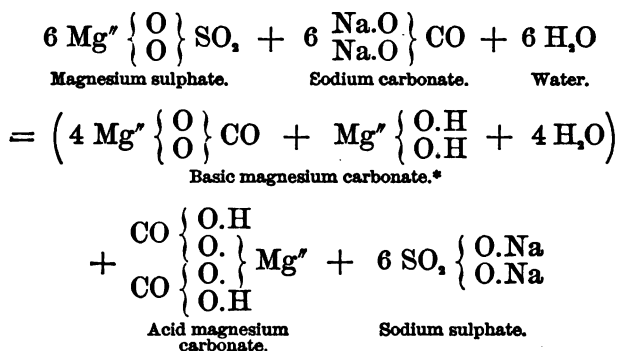
23) *Calcium monoxide.*

Solutions of this oxide also display the same behavior toward the six general reagents as that of strontium and barium monoxides; by sulphuric acid there is produced a precipitate of hydrated calcium sulphate, gypsum,  $\text{Ca}'' \left\{ \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right\} \text{SO}_4 + 2 \text{H}_2\text{O}$ , only this is not pulverulent but coarsely flocculent; it dissolves in about 400 parts of water, much easier in dilute acids, but is insoluble in alcohol. Therefore, from moderately dilute solutions the precipitation of calcium monoxide occurs only after long standing (and then in distinct little crystals), and from very dilute solutions it is not thus precipitated at all. Ammonium oxalate produces a pulverulent precipitate of calcium oxalate which is readily soluble in chlorhydric and nitric acids, but insoluble in acetic acid and oxalic acid (distinction from magnesium but not from barium and strontium).

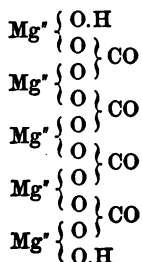
24) *Magnesium monoxide.*

The solutions of this oxide are not precipitated by sulphydric acid and ammonium sulphide, but are

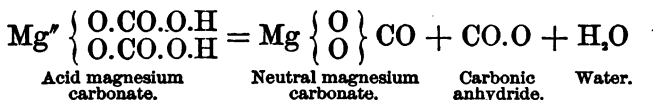
precipitated by ammonia (distinction from barium, strontium and calcium); the precipitate of magnesium hydroxide is easily soluble in ammonium chloride (see above, page 66). Sodium hydroxide solution also precipitates magnesium hydroxide; sodium carbonate precipitates basic magnesium carbonate, while a part of the magnesium remains in solution as an acid carbonate :



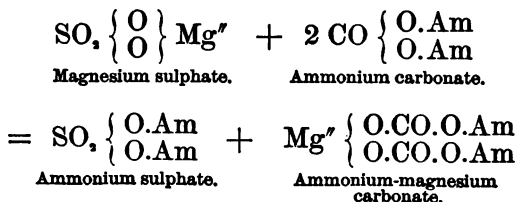
\* As thus written, the compound appears as a mixture of a neutral salt and a molecule of the free base, and four molecules of water, *i.e.*, a mixture and not a true chemical compound unless we regard it as in the category of double salt "molecular additions" (see note, page 66). The magnesium compound proper, considered as a true basic carbonate, would be thus written:



If the solution of the acid magnesium carbonate be heated to boiling, carbonic anhydride is evolved and the neutral carbonate is precipitated :

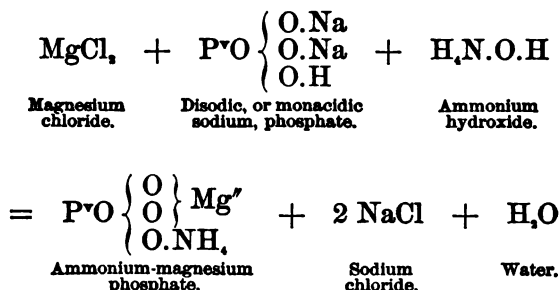


The precipitate of basic magnesium carbonate is easily soluble in ammonium chloride. Ammonium carbonate produces a precipitate in rather dilute solutions of magnesium monoxide only after some time has elapsed. Upon the addition of a considerable excess of a concentrated solution of neutral ammonium carbonate to a concentrated solution of magnesium monoxide, a crystalline precipitate of ammonium-magnesium carbonate is formed, which is almost insoluble in a concentrated solution of ammonium carbonate :



Monacidic sodium phosphate effects a voluminous flocculent precipitate of magnesium phosphate in solutions which are not too dilute ; this precipitate becomes crystalline after a while, and from dilute solutions it separates only after some time, and then it crystallizes out ; when freshly precipitated it is somewhat soluble in ammonium chloride, but the

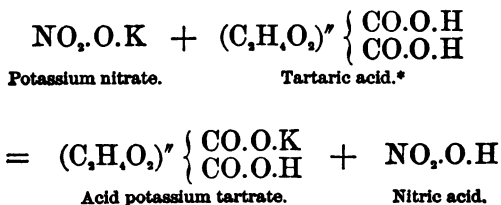
solution soon becomes cloudy, a crystalline powder separating; but if a great excess of ammonia is added, a crystalline precipitate of ammonium-magnesium phosphate is formed, insoluble in dilute ammonia:



E) METALLIC OXIDES, THE SOLUTIONS OF WHICH ARE NOT PRECIPITATED BY ANY OF THE SIX GENERAL REAGENTS.

25) *Potassium monoxide.*

Potassium is precipitated from its solution by only a few reagents. Tartaric acid produces, either at once or upon shaking the solution, a white, crystalline precipitate of acid potassium tartrate:




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\* The fully resolved formula is:

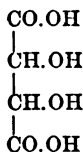
This precipitate is not insoluble in water, and therefore is not produced in dilute solutions; it is still more soluble in dilute acids, but is precipitated from such solutions by careful addition of sodium hydroxide solution. The reaction is more delicate when, instead of tartaric acid, a concentrated solution of acid sodium tartrate is employed. Further, acid solutions, especially chlorhydric acid solutions, of potassium monoxide are precipitated by platinic chloride; the crystalline precipitate is potassium-platinic chloride:  $2 \text{KCl.Pt}^{\text{IV}}\text{Cl}_6$ , difficultly soluble in water and dilute acids, insoluble in absolute alcohol.

26) *Sodium monoxide.*

Solutions of this oxide are precipitated neither by the six general reagents, nor by those special ones which precipitate potassium. It is best recognized by the extremely intensive and characteristic yellow color which it imparts to the colorless flame of a Bunsen burner.\*

27) *Ammonia.*

Although this is no metallic oxide, it should find mention here nevertheless, since its compounds are



(a dibasic acid, only the H atoms of the groups CO.OH being replaceable by metals to form salts).

\* Of course, any hot, colorless flame will answer the purpose. A good alcohol flame gives the test very satisfactorily.

so similar to those of potassium and sodium monoxides in their behavior. It is precipitated just as potassium is, and by the same reagents; it is characteristic for its salts that they are all volatile, excepting those salts of acids which are not volatile even upon ignition. Another distinguishing mark is that they all emit the characteristic odor of ammonia when treated to soda lye, even in the cold. Moreover, gaseous ammonia forms white clouds with chlorhydric acid vapors, and renders reddened litmus-paper blue.

## II. ACIDS.

### A) OXYGEN ACIDS.

a) *Solutions of their neutral salts are precipitated by barium chloride.*

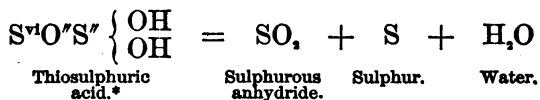
#### 1) *Sulphuric acid.*

For sulphuric acid, and for sulphates, the precipitation by barium chloride, and by lead acetate is characteristic (see pp. 70-71). Upon concentrating free sulphuric acid by evaporation it chars organic substances like paper, sugar, etc., very easily.

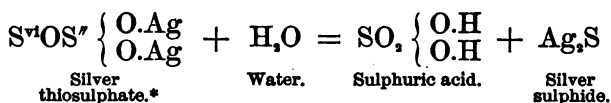
#### 2) *Thiosulphuric acid.*

The salts of this acid yield precipitates with barium chloride, lead acetate and silver nitrate; the barium thiosulphate is soluble in much hot water; the lead and silver salts are readily soluble in sodium thiosulphate. It is characteristic for this acid that it cannot exist in the free state; if other acids, as chlorhydric, sulphuric acid, etc., are add-

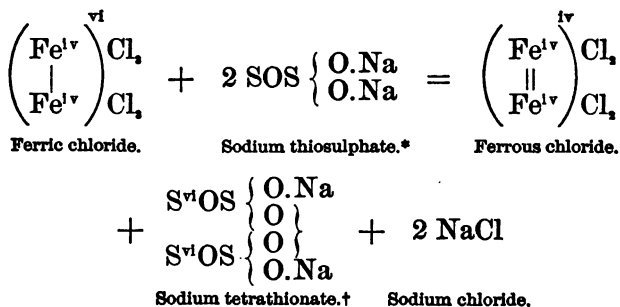
ed to solutions of its salts the acid decomposes, thus :



The thiosulphate salts of the heavy metals, especially the silver salt, decompose easily, upon being warmed or upon long standing beneath the surface of the liquid from which they were precipitated, into sulphuric acid and metallic sulphide :



With ferric chloride, the aqueous solutions of thiosulphates give a violet-red color which vanishes gradually, tetrathionic acid being formed :

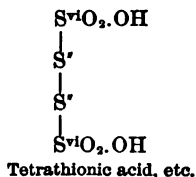
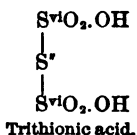
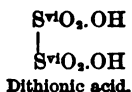


\* The more plausible formula for this acid is that given by the author on page 93.  $\text{SO}_2 \left\{ \begin{array}{c} \text{SH} \\ \text{OH} \end{array} \right\}$

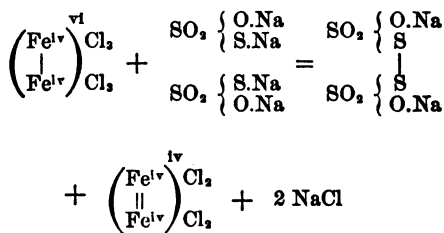
† The constitution formulas generally accepted for the polythionic acids at the present time are:

The red coloration disappears more rapidly upon the addition of a trace of copper sulphate.

3) *Chromic acid*.\*



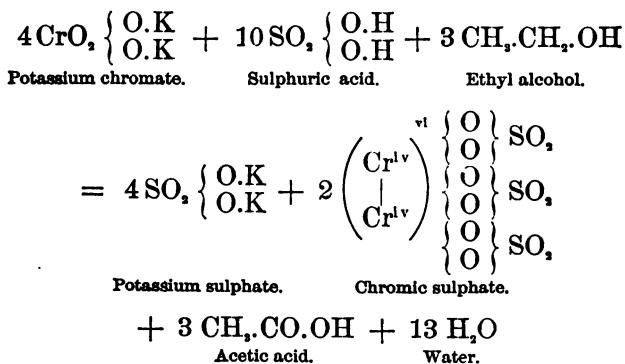
In accordance with these formulas and the one given by the author for thiosulphuric acid on page 98, this reaction becomes:



\* Acid chromates in the proper sense of the term, *i.e.*, with OH groups of the original acid still present in the salt, are not known. Under ordinary circumstances, it appears that hydroxyl, OH, cannot maintain a direct union with the radical  $\text{CrO}_2$ . Those chromates sometimes called acid chromates, but oftener bichromates or di-

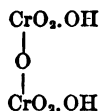


All of the salts and solutions of this acid are yellow or red ; a further characteristic is the facility with which chromic acid may be reduced to chromic oxide, whereby the color of the liquid becomes green. If sulphydric acid be conducted through a chromic acid solution, the latter turns green and, simultaneously, becomes cloudy from the sulphur which is separated (see page 56); if a chromate salt be boiled with concentrated chlorhydric acid, chlorine is evolved and chromic oxide is formed (see below, under chlorhydric acid); if, finally, organic substances are boiled with a chromate and dilute sulphuric acid, the chromic acid is likewise reduced; for example, by alcohol :




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chromates, are salts of dichromic acid (not known in the free state),



Chromic acid itself,  $\text{CrO}_3 \left\{ \begin{array}{c} \text{OH} \\ \text{OH} \end{array} \right.$  is not known in the free state, nor a proper acid salt of it.

4) *Carbonic acid*.\*

The salts of this acid are characterized by the energetic evolution of gas (carbonic anhydride) when they are brought into contact with dilute mineral acids [inorganic acids]; the gas itself is odorless, colorless, neither combustible nor capable of supporting combustion; it reddens moist blue litmus-paper feebly, and produces in lime-, or baryta-water, white, flocculent precipitates of calcium carbonate or barium carbonate, respectively.

5) *Silicic acid*.†

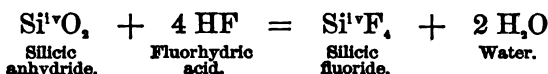
This acid is chiefly characterized by its behavior in the free state as it is separated from its compounds by stronger acids. If a silicate salt be decomposed by a small quantity of concentrated acid, there is obtained a stiff, jelly-like mass of silicic acid, which partially dissolves upon being boiled with much water (it is seldom that the silicic acid separates out as a powder). If a large quantity

\* Carbonic acid appears as a dibasic acid,  $\overset{\text{iv}}{\text{CO}}(\text{OH})_2$ , in the mineral kingdom. Its anhydride,  $\overset{\text{iv}}{\text{CO}}_2$ , has been currently called carbonic acid, which appellation has now become a misnomer, since acids are hydrogen compounds. In organic compounds carbonic acid appears not infrequently as a tetrabasic acid,  $\overset{\text{iv}}{\text{C}}(\text{OH})_4$ .

† Silicic acid functionates both as dibasic,  $\overset{\text{iv}}{\text{SiO}}(\text{OH})_2$ , and as tetrabasic,  $\overset{\text{iv}}{\text{Si}}(\text{OH})_4$ , in both organic and inorganic compounds. Possibly it has, in complex molecules, still higher basicities. It is difficult to obtain free silicic acid of constant composition, but the jelly-like product obtained by decomposing silicates by acids is, after cautious drying over  $\text{H}_2\text{SO}_4$ , approximately  $\text{SiO}(\text{OH})_2$ . The anhydride of this acid,  $\text{SiO}_2$ , has been commonly called silicic acid, just as  $\text{CO}_2$  has been called carbonic acid.

of a dilute acid be employed for the decomposition of the silicate (especially in the case of a solution of an alkaline silicate), the liberated silicic acid may remain wholly in solution, and by evaporating to a certain degree of concentration the entire liquid becomes solidified to a jelly. If this jelly-like silicic acid is dried upon the water bath it is rendered insoluble in water, but still may be easily dissolved by boiling with a solution of sodium carbonate.

In fluorhydric acid silicic anhydride is readily soluble, and the solution volatilizes, leaving no residue, since the silicic anhydride is converted into silicic fluoride gas, which is evolved :



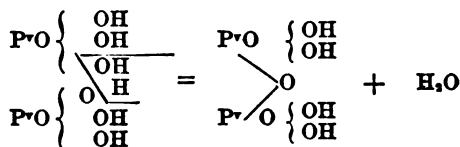
#### 6) *Phosphoric acid*.\*

Phosphoric acid displays certain peculiarities

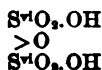
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\* The phosphoric acid of the text, the tribasic acid, is often called *ortho*-phosphoric acid in distinction from *meta*-phosphoric acid, which is monobasic, corresponding to nitric acid:  $\text{PO}_3.\text{O.H}$ .

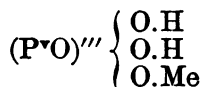
Diphosphoric acid, often called pyrophosphoric acid, is derived from condensation of two molecules of tribasic phosphoric acid, with elimination of one molecule of  $\text{H}_2\text{O}$ , thus:



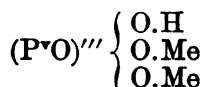
The formula indicates that it is tetrabasic. Corresponding to diphosphoric acid we have disulphuric acid:



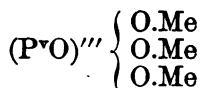
which result from its constitution. It is tribasic, *i.e.*, contains three hydroxyl groups, whose hydrogen atoms may be replaced by metals, and according as one, two, or three of those hydrogen atoms are so substituted, three different series of salts are formed :



Diacidic metallic phosphate.



Monacidic metallic phosphate.



Neutral metallic phosphate.

(The customary, but erroneous terminology for these series has been, acid, neutral and basic phosphate).

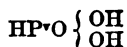
The salts of the first of the above series are all soluble in water, but this is true of only those salts

(not to be confounded with dithionic acid) and dichromic acid:



this dichromic acid is known only in its salts (see note, page 116). Salts are known which are derived from acids resulting from still higher condensations of both forms of phosphoric acid and of phosphorous acid.

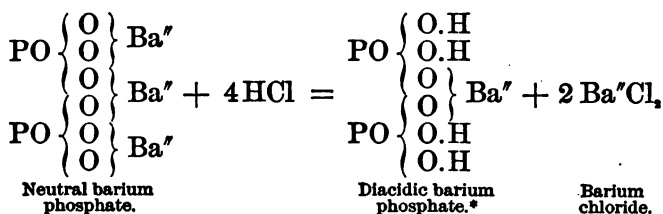
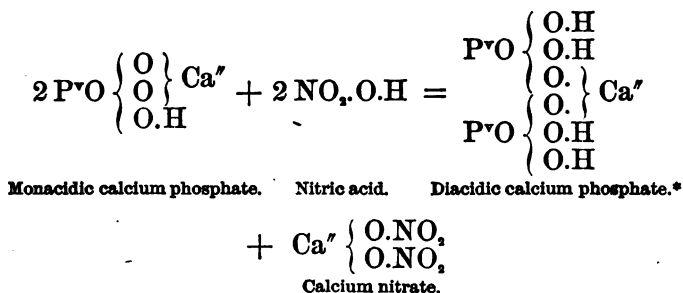
Phosphorous acid is dibasic:



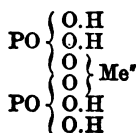
Hypophosphorous acid is monobasic:

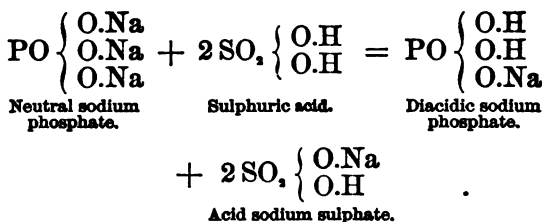


of the second and third series which are salts of an alkaline base. If salts of the second and third series be treated to acids they dissolve, in most cases, whereby a salt of the first series is produced :

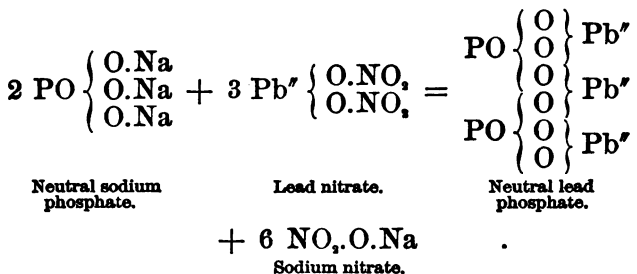


\* It might be urged that, according to note on page 88, these two salts are tetracidic since they contain four atoms of hydrogen replaceable by basic radicals. From the constitution of phosphoric acid it will be seen that it is impossible to form a diacidic salt from a *bivalent metal* and *one molecule* of the acid, since there would result:  $\text{PO} \left\{ \begin{array}{c} \text{O} \\ \text{O} > \text{Me}'' \\ \text{O.H} \end{array} \right\}$ , a monacidic salt. Hence we have to employ two molecules of the acid which gives, *referred to each single molecule* of the acid used, a diacidic salt; thus we have:

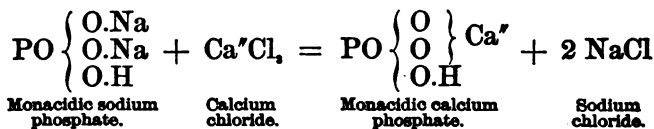




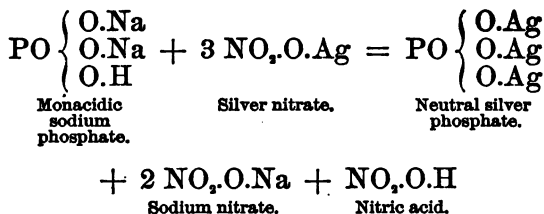
Since all of the salts of the first series are soluble, it follows that none of them can be obtained as precipitates by double decomposition; this may be done, however, with the salts of the last two series. The alkaline phosphates of the third series precipitate simply salts of the same series, from neutral solutions:



It is otherwise with the alkaline salts of the second series; these precipitate sometimes a monacidic salt and sometimes a neutral salt; the latter result obtains more especially in the case of the heavy metals. The reactions occur as follows:



and



The formation of the neutral phosphate is a consequence of the substitution not only of the two sodium atoms of the sodium salt by silver atoms, but also of the hydrogen atom by silver; this circumstance is a striking bit of evidence that this hydrogen atom exerts the same chemical function as that exerted by the two sodium atoms, *i.e.* is of basic nature; it is seen from this, moreover, that true acids, as nitric acid, in the above equation, are essentially salts, in which the hydrogen exerts the same chemical function as that exerted by the metals in metallic salts. Naturally, that which has been stated and illustrated for phosphoric acid holds good also for the monobasic and dibasic acids, which contain respectively one and two hydroxyl groups, whose hydrogen atoms are readily replaceable by atoms of metals.

With an ammoniacal solution of magnesium monoxide there is formed, by monacidic sodium phosphate, a white, crystalline precipitate of ammonium-magnesium phosphate (see page 112); arsenic acid produces a quite similar precipitate of ammonium-magnesium arsenate, from an acid solution of which, however, sulphydric acid precipitates arsenious sulphide [As<sub>2</sub>S<sub>3</sub> or As<sub>2</sub>S<sub>4</sub>]. Ferric chloride gives a

yellowish-white precipitate of ferric phosphate, easily soluble in chlorhydric acid, somewhat soluble in a solution of ferric acetate, but insoluble in acetic acid.

If to an acid solution (best, nitric acid) of a phosphate salt a nitric acid solution of ammonium molybdate in considerable excess be added, there is formed, more quickly by heating gently, a light yellow, pulverulent precipitate, consisting of molybdic anhydride, ammonia, phosphoric acid (it contains about three per cent. of phosphoric anhydride) and water. The chemical constitution of this compound is not known with certainty; it is somewhat soluble in water and in dilute acid, especially phosphoric acid; it is readily soluble in alkalies, but completely insoluble in acid liquors containing molybdic acid and ammonia.\*

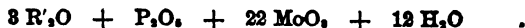
7) *Oxalic acid.*

For this acid the following reactions are important and characteristic. If oxalic acid (or one of its salts) in the dry state be heated with concentrated sulphuric acid, an evolution of gas soon ensues; if this gas be conducted into lime-water a white flocculent precipitate is produced (calcium carbonate); if the gas be collected over soda lye [strong solution of sodium

\* Debray (Bull. Soc. Chim. [2] X. 369) has assigned the formula for the composition of this compound:

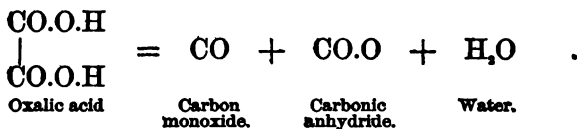


But C. Rammelsberg (Berlin Akad. Ber. 1877, 578) has later urged the formula:

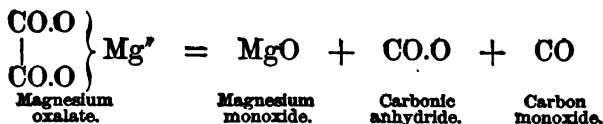
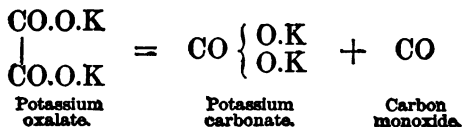




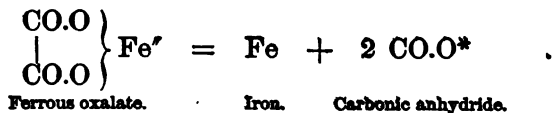
hydroxide] the carbonic anhydride is absorbed and a gas remains which, when ignited, burns with a blue flame; this gas is carbon monoxide. The decomposition of oxalic acid is completed as follows:



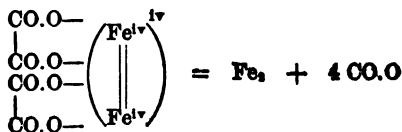
Salts of this acid, oxalates, decompose similarly:



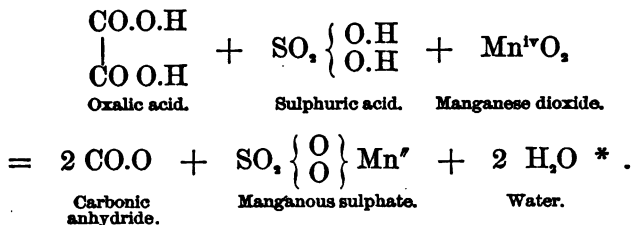
with salts of certain of the heavy metals, however, reduction occurs:



\* In harmony with the equations previously given for iron reactions, this one might be written:



By oxidation oxalic acid is converted into carbonic anhydride, as when it is heated with dilute sulphuric acid and manganese dioxide:

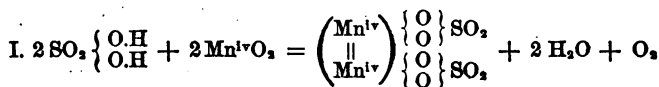


Solutions of oxalic acid and of alkaline oxalates are precipitated by calcium chloride; the precipitate is calcium oxalate, which is practically insoluble in acetic acid and in oxalic acid but is readily soluble in chlorhydric acid or nitric acid; it is therefore precipitated from this latter solution by addition of sodium acetate, since in place of free nitric acid there is produced free acetic acid, which is not a solvent for the precipitate.

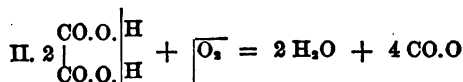
#### 8) Boric acid.†

Of the salts of this acid only those of alkaline

\* We may consider two phases of this reaction, separately:



and,



† Boric anhydride is  $\text{B}_2\text{O}_3$ . Boric acid assumes various guises. Its most simple form appears to be  $\text{BO.OH}$ , which may be regarded as the first anhydride of the form  $\text{B} \left\{ \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \right.$ . These formulas show

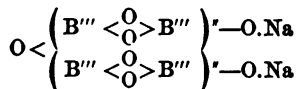
bases are soluble in water ; if a concentrated solution of such be mixed with strong chlorhydric acid, boric acid crystallizes out. This precipitate is soluble in hot water and crystallizes out again upon cooling. If silver nitrate be added to a concentrated solution of an alkaline borate, a white precipitate of silver borate is produced ; nevertheless, a dilute solution of alkaline borate yields a brown precipitate of argentic oxide, the water acting as a base with respect to the boric acid.

b) *Solutions of their neutral salts are not precipitated by barium chloride.*

9) *Nitric acid.*

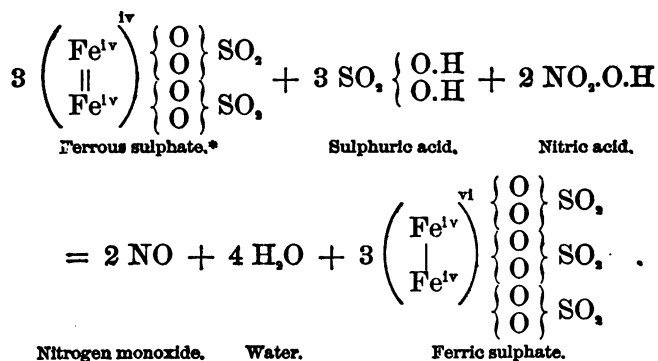
All salts of this acid, with the exception of a few basic salts, are soluble in water. The behavior of nitric acid toward the metals has been already discussed at length ; in order to recognize its presence in such combinations it is set free by the addition of concentrated sulphuric acid, and a piece of clean metallic copper is immersed in the liquid, whereupon

that the first acid is monobasic, the second tribasic. The tribasic form is especially frequent in organic compounds. Most of the common inorganic borates are salts of a complex boric acid, which may best be regarded as formed by the union of several molecules of the anhydrides of the tribasic acid. Common anhydrous borax is the sodium salt of such an acid, the composition of which admits of more than one interpretation respecting its constitution ; one of these which seems plausible is :



The corresponding acid may be regarded as derived from condensation of four molecules of the tribasic acid,  $\text{B}(\text{OH})_3$ , by elimination of five molecules of water and union of the rests.

an evolution of nitrogen monoxide occurs. The most delicate, and at the same time most characteristic, reaction for nitric acid is the brown coloration which it produces when mixed with ferrous salts. If to such a ferrous solution (acidified) nitric acid be added, and the mixture warmed, the liquid becomes colored dark brown to black, at first; suddenly, however, an energetic evolution of gas commences (nitrogen monoxide) and the liquid assumes a light reddish-yellow color, becoming transparent, when it contains only ferric oxide in solution. In this oxidation the following reaction occurs:



Before the commencement of the reaction the substances in the left-hand member of the equation were present; after its completion, those of the right-hand member; *during* the reaction, however, all of the substances of both members of the equation must have been present, and under these circumstances the nitrogen monoxide, already formed, combined with the as yet unoxidized portion of the ferrous

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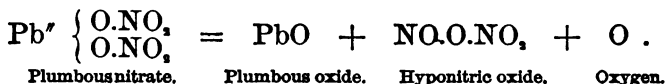
\* See note, page 6.

salt, forming the compound soluble in water with the dark-brown color; if, later, the ferrous oxide of this newly-formed compound becomes oxidized, the liberated nitrogen monoxide must escape as gas—the fluid suddenly froths. In order to recognize nitric acid by means of this reaction the best method of procedure is to mix the solution to be inspected with an equal volume of pure, concentrated sulphuric acid and then to *carefully* pour upon this hot liquid a layer of a solution of ferrous sulphate. If nitric acid be present, there is formed, either at once or after a little while, a brown ring where the two layers of liquids are in contact.

Heat effects the decomposition of all nitrates; alkaline nitrates give off oxygen at first, and a nitrite salt is left:



afterwards this nitrite is partially decomposed; the other nitrates yield oxygen and nitrous anhydride or hyponitric oxide, leaving a residue of an oxide, dioxide, *etc.* (manganese):

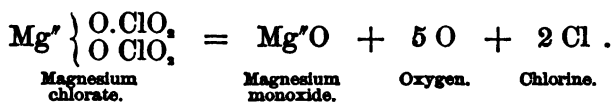


#### 10) *Chloric acid.*

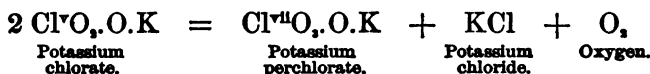
All of the salts of this acid are also soluble in water. By the agency of heat, most chlorates give off all of their oxygen, a metallic chloride remaining:



Others yield oxygen and chlorine, a metallic oxide resulting :

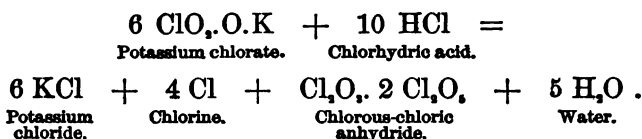


Still others decompose according to both equations. The alkaline chlorates decompose first into metallic chloride, a perchlorate salt and oxygen :

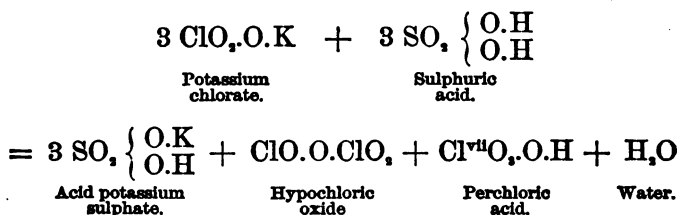


but this perchlorate decomposes afterward into metallic chloride and oxygen.

Chlorhydric acid decomposes chloric acid (and its salts) as follows :



When treated to concentrated sulphuric acid, chloric acid and its salts manifest a very peculiar deportment ; there is formed a yellowish-green gas, hypochloric oxide, which is absorbed by the sulphuric acid, producing a yellowish-brown coloration :

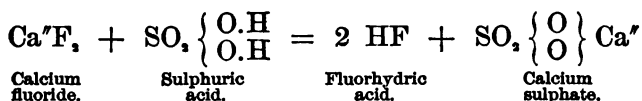


## B) ACIDS NOT CONTAINING OXYGEN. [HYDRACIDS].

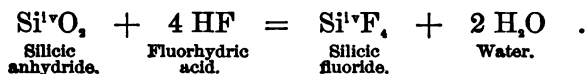
a) *Their neutral salts are precipitated by barium chloride.*

11) *Fluorhydric acid.*

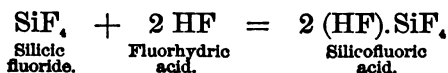
This acid is produced by the action of concentrated sulphuric acid upon metallic fluorides :



and is chiefly characterized by its reactions with silicic anhydride and with silicates. In the condition of vapor as well as aqueous acid (especially in presence of sulphuric acid) it decomposes with silicic anhydride, as follows :



If the fluorhydric acid be employed for this reaction in the state of vapor, the silicic fluoride formed is at once evolved with the excess of fluorhydric acid ; if it be employed in solution, the following compound is formed :

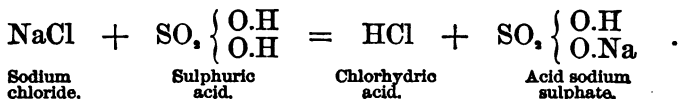


which remains dissolved in the water and, upon evaporation of the solution, decomposes into its two components and volatilizes. In the formation of gaseous silicic fluoride lies the explanation of the fact that vapors of fluorhydric acid will etch glass.

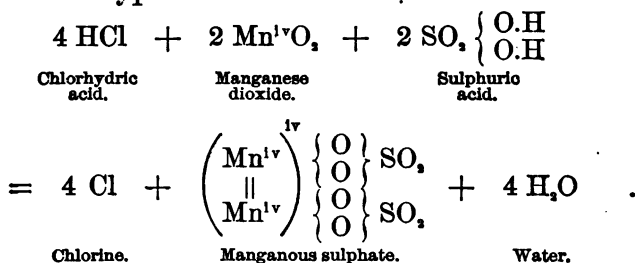
b) *Their neutral salts are not precipitated by barium chloride.*

12) *Chlorhydric acid.*

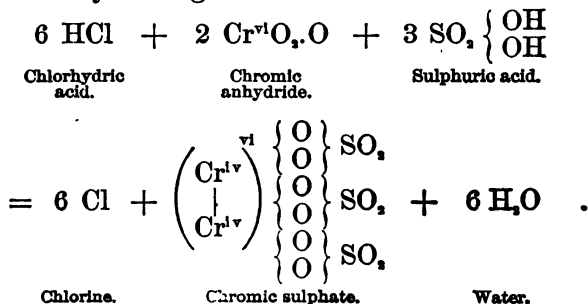
Concerning the reactions of this acid with lead and silver salts, see under these salts. The metallic chlorides, when treated to concentrated sulphuric acid, generate chlorhydric acid gas, which dissolves very easily in water, but is insoluble in concentrated sulphuric acid :



Aqueous chlorhydric acid, or a solution of a metallic chloride acidified with sulphuric acid, yields chlorine upon being boiled with manganese dioxide and other hypoxides :

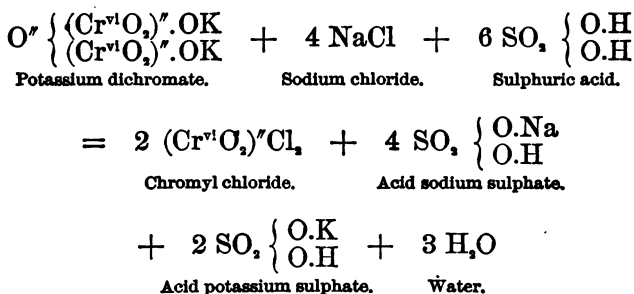


Likewise by boiling with chromic acid :

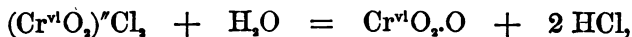




If, on the contrary, sodium chloride be fused with potassium dichromate, and the resulting product be treated to concentrated sulphuric acid, a very volatile, dark-red liquid is obtained, chromyl chloride:



This chromyl chloride, mixed with water, yields a yellow solution, with simultaneous formation of chromic anhydride and chlorhydric acid:

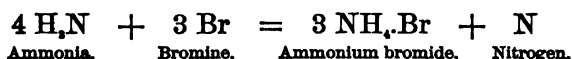


and this yellow solution remains yellow after the addition of ammonia (distinction from bromine).

### 13) *Bromhydric acid.*

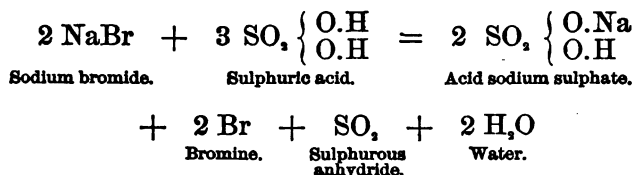
Metallic bromides manifest the greatest similarity to metallic chlorides in their chemical reactions, especially in their reactions with manganese dioxide and hyperoxides in general, chromic acid and sulphuric acid. If potassium chromate be fused with a metallic bromide and the product of the fusion be treated to concentrated sulphuric acid, there results also in this case a brownish-red vapor which condenses to a dark-red liquid, and is also dissolved by water, yielding a yellow-colored liquid; but this

vapor is pure bromine, and the aqueous solution of it is decolorized by ammonia:



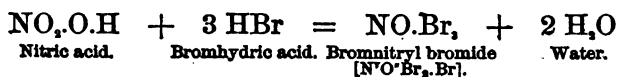
This reaction, which [for bromine] takes place in the sense of the equation given for aqueous chlorhydric acid and chromic anhydride, is very well adapted for the detection of small quantities of chlorine in presence of bromine.

If a metallic bromide be treated to concentrated sulphuric acid, bromhydric acid gas is evolved which fumes strongly in moist air; at the same time a certain quantity of free bromine is produced:



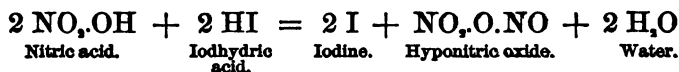
Bromine is expelled from its combinations with hydrogen or the metals by free chlorine (see p. 7). Concentrated nitric acid generates with bromides reddish-brown vapors which are probably mixtures of nitrosyl bromide [  $\text{N}^{\text{viii}}\text{O}^{\text{v}}\text{Br}$  ], tetrabromhypo-

nitric oxide [  $\left( \begin{array}{c} \text{N}^{\text{viii}} \\ | \\ \text{N}^{\text{v}} \end{array} \right) \left\{ \begin{array}{l} \text{O}^{\text{v}} \\ \text{Br}_4 \end{array} \right.} \right]$  and bromnitryl bromide [  $\text{N}^{\text{v}}\text{O}^{\text{v}}\text{Br}_3\text{Br}$  ] :

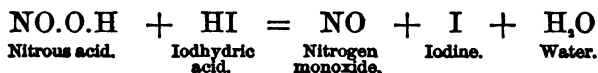


14) *Iodhydric acid.*

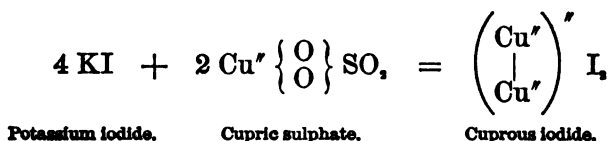
The metallic iodides also display a great similarity to the metallic chlorides; they react like the latter with chromic acid and hyperoxides. With concentrated sulphuric acid they react like the bromides, *i.e.*, iodine is liberated, though no iodhydric acid is formed. Concentrated nitric acid also liberates iodine:



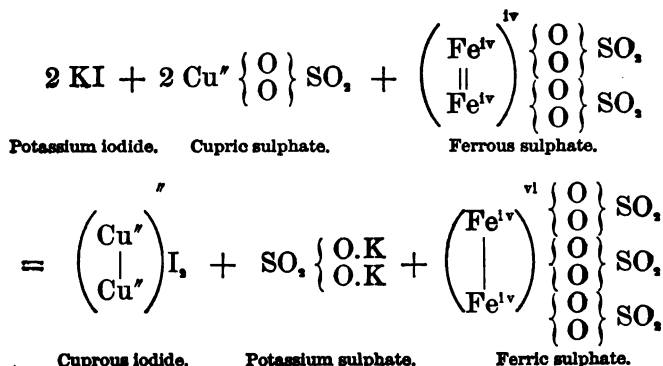
Nitrous acid acts just as nitric acid does, even when greatly diluted (distinction from bromine and chlorine):



Both free bromine and free chlorine expel iodine from its compounds (see p. 7). If cupric sulphate be added to a solution of potassium iodide, cuprous iodide separates, and iodine is liberated:

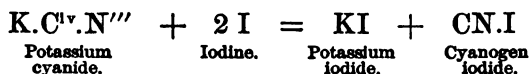


If ferrous sulphate be present at the same time, no iodine is liberated, but the ferrous oxide is converted to ferric oxide :



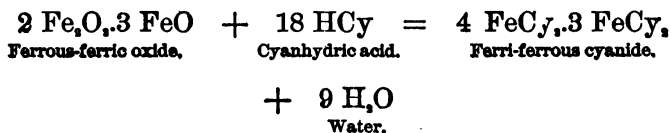
### 15) *Cyanhydric acid.*

The metallic cyanides and cyanhydric acid (prussic acid) are closely related, in many respects, to the metallic chlorides, *etc.* The most important features of their general behavior and some special reactions have been already mentioned, so that only the following remarks need be made. Chlorine, bromine, and iodine do not liberate cyanogen from its compounds, but produce respectively cyanogen chloride, bromide, and iodide, often with attendant intense brown coloration and total decomposition in other directions :



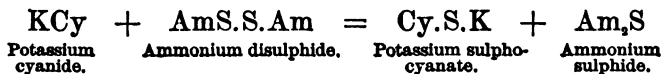
The following two reactions are especially characteristic: if some solution of ferrous-ferric oxide (such as a mixture of ferrous sulphate and ferric

chloride) be added to a liquid containing cyanhydric acid, and then sodium hydroxide solution be added in slight excess, a muddy precipitate is produced which dissolves in dilute chlorhydric acid, leaving ferri-ferrous cyanide, Berlin blue, undissolved. The reaction evidently runs as follows :



(for the rational formula of the Berlin blue, see under ferric oxide, p. 105.)

If a solution of potassium cyanide be heated with yellow ammonium sulphide (polysulphide), the liquid rapidly becomes colorless, potassium sulphocyanate being formed.



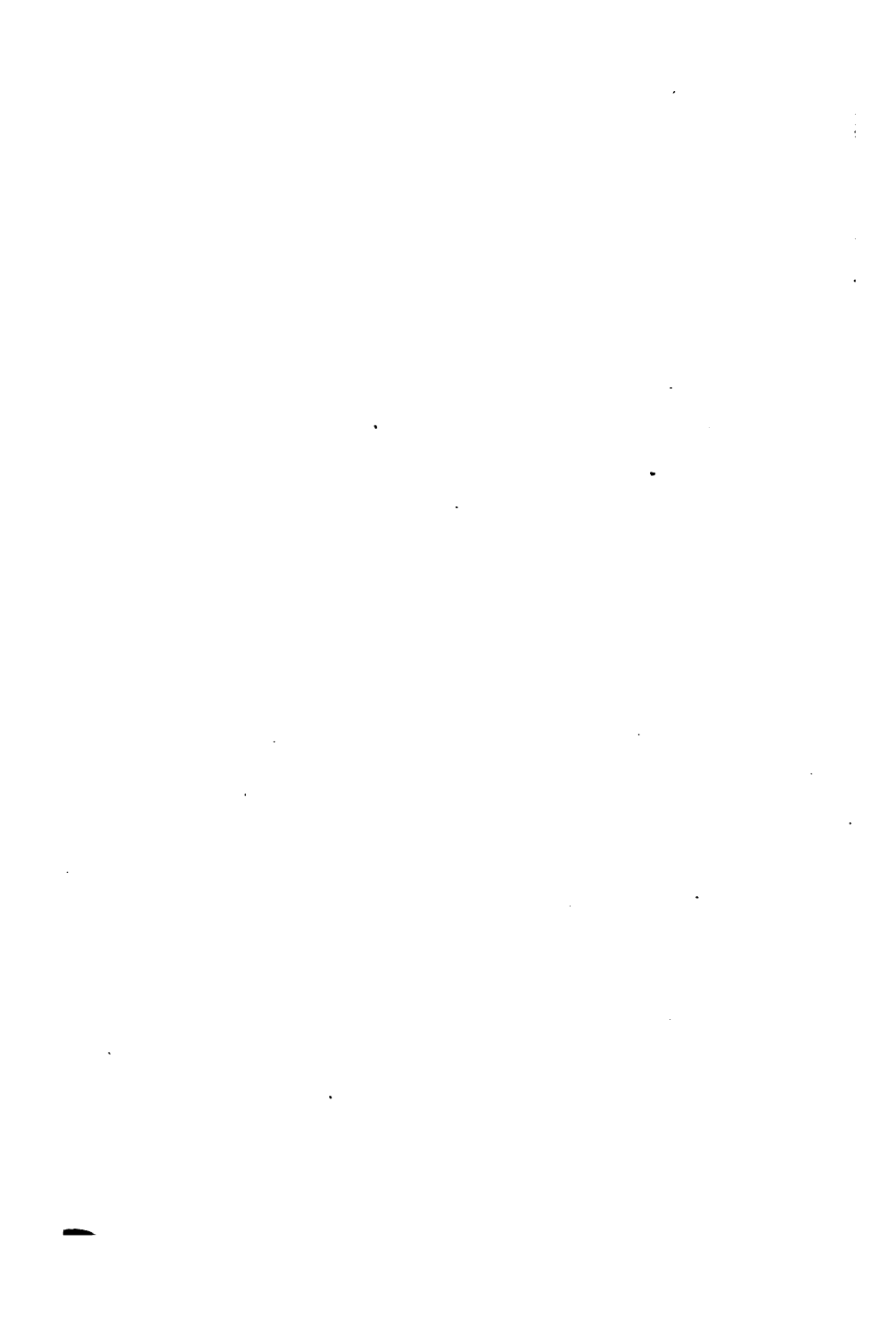
The potassium sulphocyanate may be easily detected by evaporating the liquid to dryness on the water-bath, thus expelling all ammonium sulphide, dissolving the residue in water with the addition of a few drops of dilute chlorhydric acid and adding ferric chloride ; a blood-red coloration indicates the presence of potassium sulphocyanate.

#### 16) *Sulphydric acid.*

The behavior of this acid as well as of the metallic sulphides has been already given in sufficient detail. Especially characteristic for sulphydric acid is its odor ; its power to blacken paper soaked

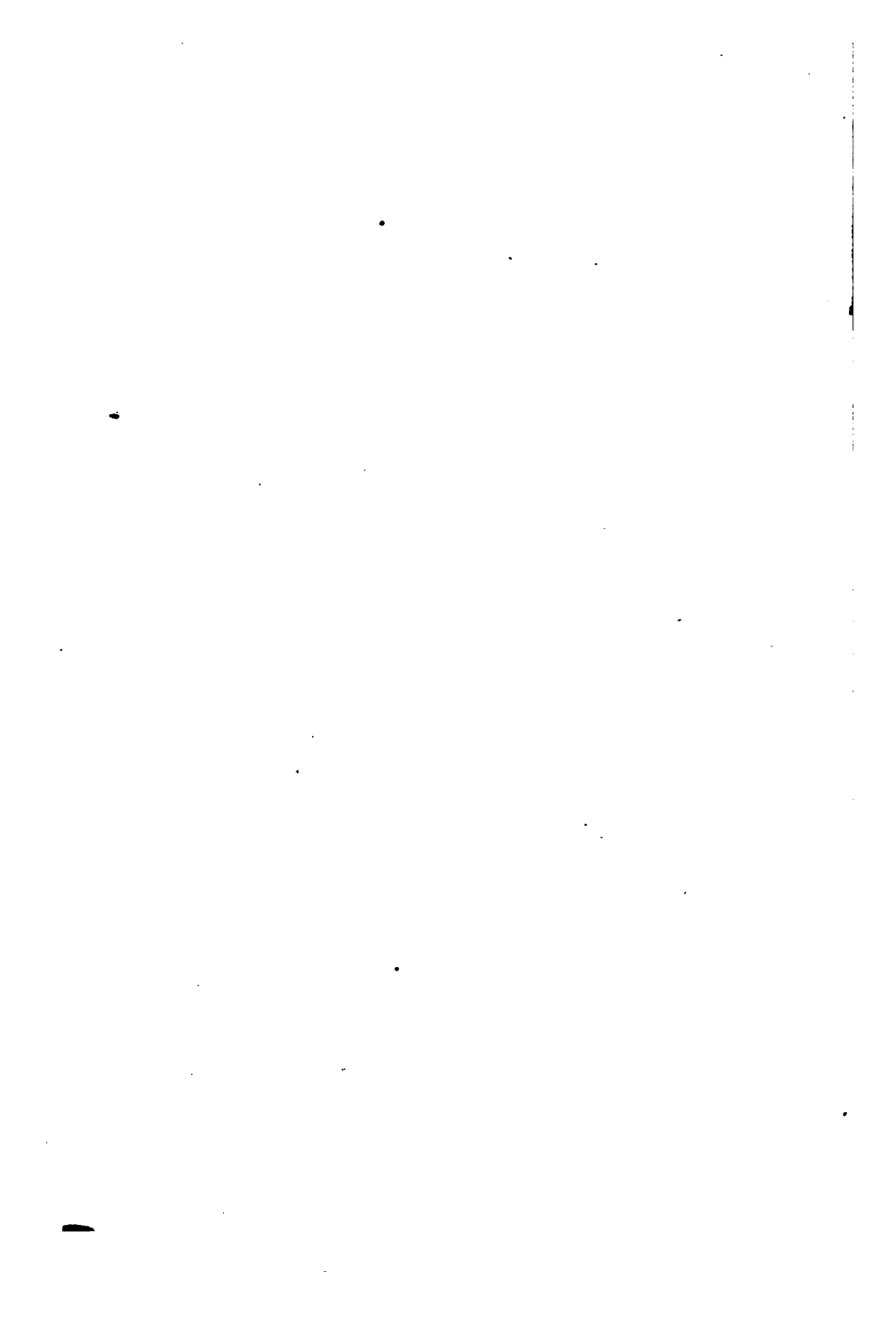
in lead or silver solutions (the surface of the paper assumes a metallic luster by this reaction) ; that it is inflammable, burning with a blue flame, yielding the odor of burning sulphur (sulphurous anhydride); that, in contact with many reducible compounds, it is decomposed with a separation of sulphur.

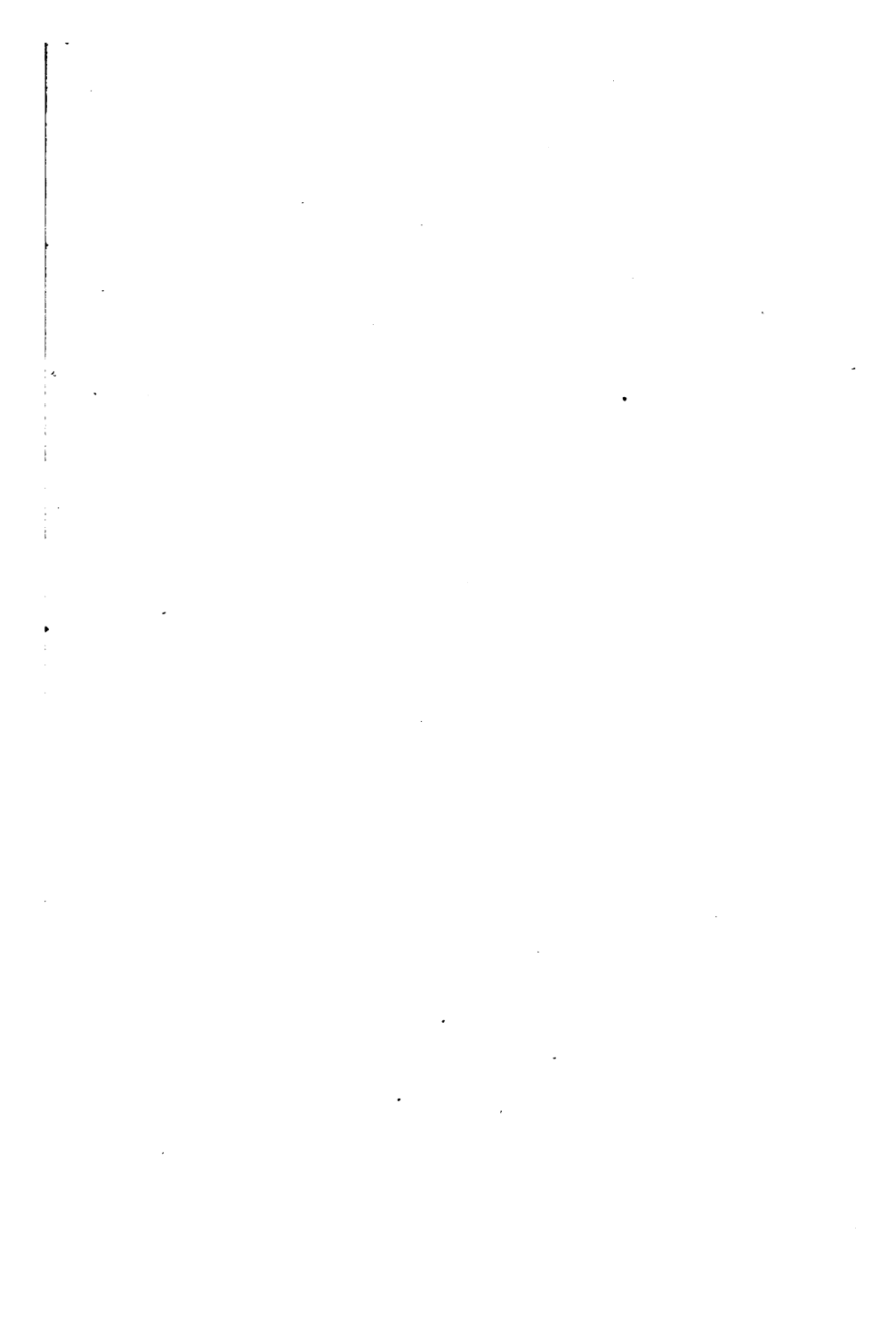


















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